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THE BEHAVIOR OF MAGNESIUM IN POTASSIUM DICHROMATE SOLUTIONS

A. G. Samartsev and E. I. Levitina

The active behavior of magnesium in aqueous solutions of electrolytes can be explained on the basis of its belonging to the group of electronegative metals. Passivity of magnesium is observed in alkaline solutions [1], as well as in chromate and fluoride salt solutions, in which layers of poorly-soluble compounds are formed at the magnesium surface.

Upon heating magnesium in potassium dichromate solution to the boiling point, there is observed after several minutes of immersion a small evolution of gaseous hydrogen, which subsequently ceases. The metal surface undergoes no noticeable changes upon further and prolonged standing in the solution. Under such conditions, the magnesium becomes passive, being covered with a thin protective layer.

Introduction into the potassium dichromate solution of some neutral salts which do not affect the acidity of the solution affects markedly the behavior of the metal: magnesium begins to dissolve extensively, hydrogen being displaced, and a visible protective layer is formed on the surface. Thus, under the influence of neutral salts, the metal surface becomes activated.

Up to the present time, this phenomenon has received but little study, although it has been known for a long time [2]. Introduction of activating salts into potassium dichromate solution is used widely in technology for the production of protective layers upon magnesium and its alloys [3].

In the present work, the growth rate for the protective layers on magnesium in potassium dichromate solution containing additives has been studied.

For the experiments, samples of pure magnesium (99.96%) in the form of sheets were used. The surface of one sample amounted to 30 cm². Experiments were carried out with 10% potassium dichromate solution, in which were introduced neutral salts as activating additives. The weight of layer produced was determined. Weighings were carried out on an analytical balance to within an accuracy of 0.1 mg. To determine the layer weight, the latter was removed from the sample by dissolving in concentrated alkali at elevated temperature. The solution, containing 600 g sodium hydroxide/liter, was used at the boiling temperature (125°). Soaking time of the metal in the solution was 30 seconds. Experiments indicated that by such procedure any error due to removal of the layer, apparently by dissolution of the metal, can be ignored. For coatings weighing 5-10 mg the error of determination did not exceed 5%.

In Fig. 1 is given the weight of coating used, as formed on magnesium in 10% potassium dichromate solution, versus the concentration of sodium sulfate introduced into solution. Experiments were carried out at 80°. As shown by measurements carried out with a glass electrode, the acidity of the solution did not change upon introduction of sodium sulfate.

In pure potassium dichromate solution under the same conditions, no coatings visible to the eye were formed on the metal, and samples of the metal did not change in weight. Upon introducing sodium sulfate, a violent evolution of hydrogen from the metal surface of the sample was observed: Light-brown non-uniform coatings were formed on the metal surface in solution containing 5 g of sodium sulfate/liter. With increased concentrations of sodium sulfate, up to 20 g/liter and higher, the resulting coats were of uniform dark-brown color.

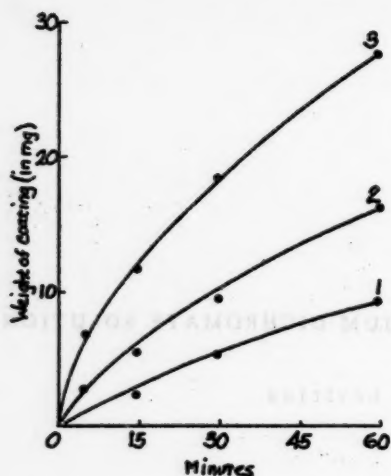


Fig. 1. Effect of activating additive (sodium sulfate) upon protective coating growth on magnesium in 10% potassium dichromate solution. Temperature of solution, 80°. 1) 5 g/l Na_2SO_4 ; 2) 20 g/l Na_2SO_4 ; 3) 100 g/l Na_2SO_4 .

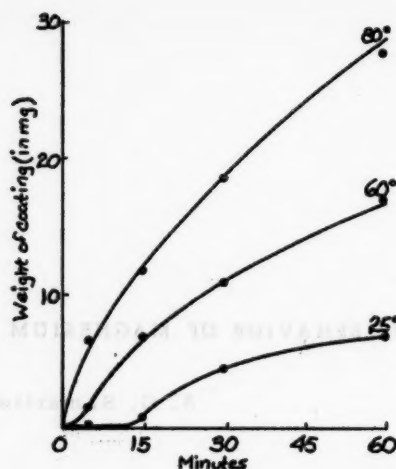


Fig. 2. Effect of activating additive upon the growth of protective coating on magnesium in 10% potassium dichromate solution relative to temperature. Solution containing 100 g sodium sulfate per liter.

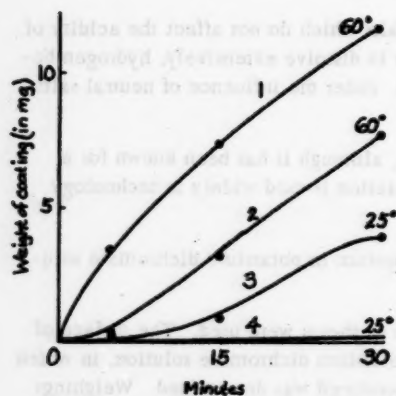


Fig. 3. Protective coating growth on magnesium in 10% potassium dichromate solution with respect to metal surface condition. Solution containing 100 g sodium sulfate/liter. Temperatures, 60 and 25°. 1, 3) Polished samples without added chemical processing; 2, 4) samples pretreated in potassium dichromate solution.

With increase in time, the rate of growth of the coating decreased. The process thus possessed a decelerating character. The coating formed apparently inhibits the rate of chemical reaction between metal and solution.

Analogous phenomena were observed with the chlorides, phosphates and fluorides of the alkali metals introduced into the potassium dichromate solutions. In potassium dichromate containing chlorides, coating formation is accompanied by centers of disintegration of the metal. In solutions containing phosphate, the coating increased at a lower rate than for solutions containing sulfates. The action of fluoride salts depended upon their concentration in the solution. Addition of small amounts of fluoride (0.1 g sodium fluoride/liter) acted in a manner similar to that for sulfate and phosphate salts; in such cases, metal surface coatings of considerable thickness were formed, brown in color. With an increased content of fluoride, however, there were formed colorless coatings of magnesium fluoride on the metal. Evolution of hydrogen on the metal sample ceased rapidly in this case.

The effect of activating additives depends considerably upon the acidity of the potassium dichromate solution. The rate of metal solubility decreases sharply with decrease in acidity, and hence the rate of coating growth is slowed down.

The temperature of the solution exerts a great influence upon the coating growth. Corresponding data for 10% potassium dichromate solution, containing 100 g sodium sulfate per liter, are given in Fig. 2. Experiments were carried out at 25, 60 and 80°.

As can be seen from Fig. 2, the rate of growth of protective coating decreases with decrease in temperature of solution. There was observed at lower temperature an induction period in coating formation during initial stages of the process. It was most evident at 25°. The induction period is apparently related to the presence of a natural oxidation layer on the metal surface.

The rate of coating growth on magnesium in potassium dichromate solution containing sodium sulfate (at pH 3.2) decreases sharply if the metal sample is suspended beforehand in potassium dichromate solution heated to boiling and without additives. The experimental data are presented in Fig. 3. If experiments are carried out at 25°, then complete passivation of metal is observed, no visible coating being formed in this case (Curve 4). For samples not pretreated in dichromate, there appears, as was indicated, a relatively thick layer. The marked effect of preliminary passivation (Curves 1 and 2) is clearly observed at 60°; it is first of all expressed by the presence of an induction period during the initial stage of coating growth. Preliminary passivation was carried out in 10% potassium dichromate solution by boiling for 30 minutes.

Thus magnesium was found to be passive in solutions of potassium dichromate even at boiling temperature; on the surface is formed a thin, invisible passivity-inducing layer, which appears during the induction period in the above-described experiments.

An explanation for the action of the activating salt should be sought for in the fact that for anions of these salts the film forming is found to be permeable. Dissolution of metal is the consequence, accompanied by violent evolution of hydrogen and by growth in thickness of the film.

The ability of various anions to penetrate through the protective layer of metals has received but little study. It has been established that chloride ions possess high permeability [4].

The growth mechanism for the protective layer on magnesium in chromate salt solutions can be schematically presented as follows. The magnesium going into solution reduces the hexavalent chromium to trivalent. The solution is rendered alkaline in the area of the metal surface, and trivalent chromium compounds of low solubility separate from solution, forming a protective layer on the metal surface. Magnesium as well as hexavalent chromium can enter into the composition of the film. In the process of coating growth, part of the metal becomes lost to the solution and does not participate in construction of the coating.

SUMMARY

1. Magnesium is rendered passive in potassium dichromate solutions, both at room temperature and at the boiling point. Passivity is conditioned by the formation of a thin, invisible, protective coating, composed of poorly-soluble compounds.
2. Introduction of "activating" salts into the solution partially destroys passivity of the metal, and leads to formation of a surface layer of considerable thickness, varying in color from yellow to brown.
3. The effect of activating salts depends in great part upon the temperature and acidity of the solution.
4. Activation of the salts introduced is apparently connected with the permeability of the protective layer to anions of these salts.

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* T.p. = C. B. Translation pagination.

THE THERMAL EFFECT OF THE $\text{PbCl}_2(\text{cr}) + \text{Cl}_2(\text{g}) \rightleftharpoons \text{PbCl}_4(\text{liq})$ REACTION

AND THE STANDARD HEAT OF FORMATION OF $\text{PbCl}_4(\text{liq.})^*$

F. Ya. Kulba

Many investigators have attempted in vain to prepare PbCl_4 by direct oxidation of lead chloride with chlorine under various conditions. In the author's preceding article [1], lead tetrachloride was characterized from a chemical viewpoint. Desiring to study in detail the conditions for formation of this compound, the authors decided to measure its heat of formation from lead chloride and chlorine, and to calculate the standard heat of formation for $\text{PbCl}_4(\text{liq.})$ from elementary substances.

As the basis for thermochemical measurements, the interaction of lead tetrachloride with excess iodine dissolved in carbon tetrachloride was used.

EXPERIMENTAL

1. Selection of Calorimeter System and Accuracy of the Measuring Apparatus

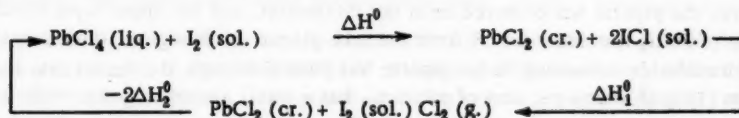
The stability of lead tetrachloride and its solutions prepared by suitable procedure (in CCl_4) at 25° made it possible for the authors to carry out the thermochemical measurements under standard conditions.

Allowing for the fact that preliminary experimental results indicated for orientation that the reactions $\text{PbCl}_4(\text{liq.}) + \text{I}_2(\text{sol.}) \rightarrow \text{PbCl}_2(\text{cr.}) + 2\text{ICl}(\text{sol.})$, and $\text{I}_2(\text{sol.}) + \text{Cl}_2(\text{g.}) \rightarrow 2\text{ICl}(\text{sol.})$, under investigation, are accompanied by a considerable thermal effect, the author decided to select for his calorimeter system the standard calorimeter of Boze-Vrevsky, described in the works of Vrevsky [2], Mischenko, and other investigators [3, 4, 5].

As calorimeter container, a thin-walled, glass beaker, 405 ml in volume, served. Its ratio of height to diameter was 1.4. The calorimeter cover was made of "textilite" plastic, 0.5 mm in thickness. The measuring instruments (Beckmann thermometer, milliammeter, and millivoltmeter) were checked beforehand. Accuracy of temperature readings amounted to $\pm 0.001^\circ \text{C}$. Amperage and voltage were, respectively, measured to within an accuracy of $\pm 0.005 \text{ A}$ and $\pm 0.002 \text{ V}$. Accuracy of the secondmeter was $\pm 0.2 \text{ sec}$.

2. Reaction Cycle

Being unable to carry out in the calorimeter a direct synthesis or decomposition of lead tetrachloride, the heat of formation was determined according to the following cycle:



According to the law of Hess:

$$\Delta H^0 + \Delta H_1^0 - 2\Delta H_2^0 = 0.$$

Hence,

$$\Delta H^0 = 2\Delta H_2^0 - \Delta H_1^0.$$

* Throughout the article, the following abbreviations are used: cr. = crystalline, g. = gas, liq. = liquid, sol. = solution.

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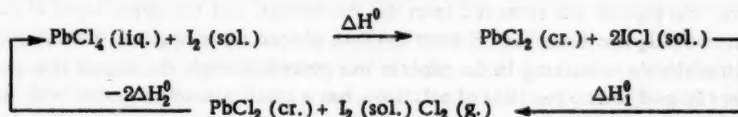
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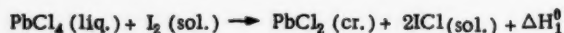
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Hence,

$$\Delta H^0 = 2\Delta H_2^0 - \Delta H_1^0.$$

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Thus, to calculate the thermal effect of interest to us, the heats of reaction given in the cycle under standard conditions had to be measured:



and



3. Procedure for Measuring the Heat of $\text{PbCl}_4 (\text{liq.}) + \text{I}_2 (\text{sol.}) \rightarrow \text{PbCl}_2 (\text{cr.}) + 2\text{ICl} (\text{sol.})$ Reaction

Since introduction of lead tetrachloride in solution into the calorimeter container is difficult from the point of view of isothermicity of the solutions mixed, the author preferred to introduce PbCl_4 in the free state, particularly since the high thermal effect of the reaction makes it possible to neglect such a small amount. Difficulty remained only in the fact that because of instability of the lead tetrachloride in air, it could not be introduced into the calorimeter by ordinary procedure.

After a number of preliminary experiments, the author decided to use for this purpose an apparatus shown in the drawing, consisting of a U-shaped pipette, 3 ml in volume, a small funnel, and a cylindrical glass tube, the top internal wall of which was ground. The funnel was equipped with a long outlet tube reaching almost to the surface of the solution in the calorimeter, and serving at the same time as a stopcock for the cylindrical tube. Its external conical wall was ground and firmly sealed the tube opening. The upper part of the funnel was cylindrical and fitted tightly to the ground tube.

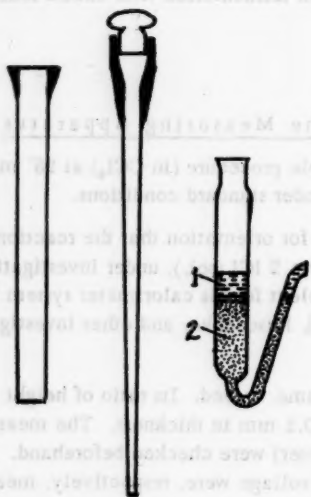


Fig. 1. Apparatus for introduction of PbCl_4 into calorimeter. Explanation in text.

The cylindrical glass tube with funnel placed inside was vertically and tightly fitted into the opening of the calorimeter cover. In assembled form, together with the funnel, it was of such height as to protrude above the upper calorimeter wall not more than 1-1.5 cm. By such an arrangement of the apparatus, the walls of the funnel possessed, at the moment of thermal equilibrium of the system, the temperature of the calorimeter casing, because of which fact heat exchange with lead tetrachloride at its moment of introduction into the calorimeter was avoided. Prior to start of the experiment, the lead tetrachloride (2), introduced into the pipette and covered with a film of concentrated sulfuric acid (1) (Fig. 1), was placed in a thermostat, in which it was heated to the experimental temperature

(25° C). At the proper time, the pipette was removed from the thermostat, and the upper layer of sulfuric acid along with a small amount of PbCl_4 was decanted off from the tube placed at an angle. Immediately following this operation, the lead tetrachloride remaining in the pipette was poured through the funnel into the calorimeter beaker with iodine solution (12 g of iodine per liter of solution), but a small amount together with the sulfuric acid layer at the top was left in the pipette to avoid getting acid into the reaction mixture. The funnel was immediately removed subsequent to the operation, since otherwise the lead tetrachloride remaining on the wall would disintegrate, by such action disturbing the normal temperature course in the final experimental phase. After removal from the funnel, the tube was immediately covered with a ground stopcock.

Each determination of thermal effect consisted actually of two separate experiments: an elevation in temperature was first measured, corresponding to a specific amount of PbCl_4 reacting with the iodine, and then after cooling the calorimetric beaker contents, the temperature rise corresponding to a specific quantity of electrical energy passed through the mercury spiral measured. The quantity of lead tetrachloride entering into reaction was found each time by analysis according to the sulfate method, after having taken the calorimetric measurements.

4. Calculation of the thermal Effect of the Reaction Carried out According to the

$$\text{Formula } \Delta H_{298}^0 = \frac{Q \cdot m \cdot \Delta \theta}{a \cdot \Delta T}$$

where ΔH_{298}^0 is the heat of reaction, calculated for 1 mole;

m is the molecular weight of PbSO_4 , equal to 303.28;

a is the weight of lead sulfate found analytically;

$\Delta \theta$ is the temperature rise at expense of heat evolved during reaction time;

ΔT is the temperature rise while heating the calorimeter contents by electric current;

Q is the quantity of heat (in calories) given up by the mercury spiral during passage of the electric current.

The data obtained by the author are presented in Table 1.

TABLE 1

Thermal Effect of the Interaction of Lead Tetrachloride with Iodine Dissolved in Carbon Tetrachloride

Indicators	Symbols	Experiment No.				
		1	2	3	4	5
Weight of iodine solution	B	499.7	499.8	499.7	498.5	499.1
Weight of PbSO_4	a	2.0804	2.2507	2.4181	2.1726	2.3391
Temperature rise.	$\Delta \theta$	1.157	1.228	1.323	1.195	1.281
Correction for radiation during reaction ...	$\Delta(\Delta \theta)$	0.031	0.039	0.032	0.028	0.027
Temperature rise.	ΔT	1.425	1.003	1.021	0.975	0.991
Correction for radiation during passage of electric current through spiral	$\Delta(\Delta T)$	0.050	0.020	0.020	0.013	0.030
Amperage	I	2.8040	2.8980	2.9138	2.8396	2.8580
Voltage.	E	2.8126	2.8980	2.9225	2.8405	2.8614
Duration of current flow (in sec.)	t"	90.2	60.2	60.4	60.6	60.6
Quantity of heat (in calories) evolved during the experiment, due to the reaction.	Q	168.47	119.74	121.81	115.76	117.36
Thermal effect of the reaction.	ΔH_{298}^0	-19941*	-19754	-19795	-19805	-19672
Average value	ΔH_{298}^0	-19793 cal/mole				
Average absolute error	$\Delta(\Delta H_{298}^0)$	+ 64 cal/mole				
Average relative error	-	+ 0.32%				

5. Procedure and Results of Measurements of Heat of Formation of Iodine Chloride From Gaseous Chlorine and Iodine Dissolved in Carbon Tetrachloride

a) Starting products. The iodine solution was prepared of same concentration as in preceding measurements, i.e., 12 g of iodine per liter of solution. After preparation of the solution, the iodine concentration was determined accurately by titration. The iodine and carbon tetrachloride were purified thoroughly each time.

Chlorine was taken from a tank, but was first passed through tubes of concentrated sulfuric acid to absorb moisture. Chlorine dried in this manner was analyzed to determine the total impurities in it (CO_2 , N_2 , CO , O_2), collectively, since under the author's experimental conditions none of the separate components could interact chemically with the calorimeter contents, and could only cause an undesirable change of enthalpy in the system upon passing through the solution (due to evaporation of carbon tetrachloride).

The total impurities not absorbed by 10% KI solution constituted on the average (three measurements) 0.2 ml for 132.5 ml of chlorine, or 0.15% (burette for the analysis graduated with mercury). Since approximately 200 ml of chlorine was introduced into the calorimeter during the experiment, the volume of unabsorbed gases, therefore, can be considered equal to $200.0 \cdot 0.0015 = 0.3$ ml, and the volume of carbon tetrachloride evaporated by same to be even less. The quantity of heat used by the system for this evaporation was beyond the range of accuracy of the calorimetric measurements, because of which errors from these heat losses were not introduced.

* Exothermal effect is -; endothermal effect is +.

b) Apparatus for introducing chlorine into the calorimeter. It was established by preliminary experiments that in order to produce an increase of 1° in temperature at the expense of the reaction, it is necessary to introduce about 200 ml of chlorine into the calorimeter.

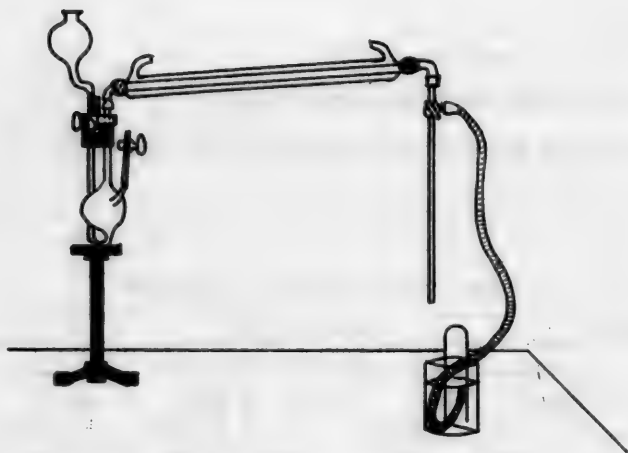


Fig. 2. Apparatus for heating chlorine prior to its introduction into the calorimeter. Explanation in text.

It was not feasible in the case of the calorimeter, however, to set up a container of such volume directly in the calorimeter beaker or in the calorimeter case; the author, therefore, constructed the apparatus in such manner that it permitted carrying out of chlorine pre-heating to the experimental temperature of the thermostat. It was borne in mind, however, that the exact quantity of chlorine entering into reaction is determined not by direct measurement of its volume in the apparatus, but by titration of the calorimeter contents after the experiment.

The main part of the apparatus (Fig. 2) consisted of two round glass containers inter-connected by a glass tube of about 0.4 cm diameter. The upper outlet tube of the bottom container consisted of a thick-walled capillary, ending at the top with a ground exterior. The outlet tube was closed by a three-way stopcock, and

the connecting tube by a standard stopcock. The lower container was filled with chlorine before the experiment, the upper reserved for concentrated sulfuric acid, by means of which chlorine was displaced from the lower container to the calorimeter. The outlet tube of the lower container was connected by a ground surface to the capillary tube bent at a 90° angle, which in its turn was also connected by a ground surface to the container full of chlorine, with a thin-walled capillary tube immersed in the calorimeter solution and fastened to the cover of the latter. The calorimeter tube was closed at its upper part by a three-way stopcock and was ground at the top. The tube connecting container with calorimeter was placed in a glass sleeve, through the inside of which circulated water, entering from the calorimeter case into the thermostat. The container with chlorine was fastened in such way that it could be freely rotated in any direction, which made it possible to set the openings of the ground stopcock in that position which allowed hermetic connection with the bent tube which was slipped on from above.

The container was filled with chlorine in the upturned position. The chlorine which entered through the outlet tube displaced the air rapidly and completely. (Complete displacement of air was checked with KI.) The stopcocks closing the container were closed with continuous chlorine flow, in such sequence that the three-way stopcock was the last to be closed.

The temperature at which the container was filled with chlorine was approximately 5° below the thermostat temperature.

Because of this fact, chlorine before the start of the experiment was heated in a thermostat at 25° C (temperature tested by thermometer placed inside container with chlorine) and was at all times under some pressure, which served to effect automatic displacement of air from the horizontal tube connecting chlorine-filled container with calorimeter. It was done as follows. Before start of the experiment, the three-way stopcock of the tube lowered into the beaker with solution was set in such a way that the end of the tube was connected with the outlet of the horizontal connecting tube, and through a second three-way stopcock, to the air. Chlorine in the container, which was under a slight pressure at this time, escaped outside and displaced air from the tubes in the space between the two three-way stopcocks. Since, along with air, a small amount of chlorine also escaped, to avoid pollution of the surrounding atmosphere the authors led this mixture of gases (chlorine and air) into a pneumatic bath through a tube connected with the side outlet of the tap. Thus heat losses were avoided which would have inevitably taken place as a result of carbon tetrachloride evaporation while passing through a solution of the air trapped in the tubes.

The chlorine was introduced into the carbon tetrachloride solution of iodine (in the calorimeter), together with an 11th reading of the temperature from start of the experiment. During the time interval between 10th and 11th readings of temperature concentrated sulfuric acid was poured into the upper container which had been in the thermostat for one hour prior to this operation. Immediately after pouring in the sulfuric acid, the three-way stopcock was turned in such manner that chlorine escaping from the container could be directed into the calorimeter. Simultaneously with the 11th reading of temperature, the stopcock in the lower part of the container with sulfuric acid was opened. The latter flowed evenly into the lower part of the container with chlorine, displacing it gradually into the calorimeter.

Inflow of chlorine into calorimeter was interrupted at the desired moment by an appropriate turn of the three-way stopcock.

The amount of heat corresponding to the temperature rise upon passing a specific amount of chlorine into the calorimeter was found similarly as for the heat effect measured in the first reaction.

c) Analytical method and results of measurements. The amount of chlorine interacting with iodine, and hence the amount of iodine chloride formed, was determined by titration with sodium thiosulfate. In this connection, interaction of chlorine with iodine proceeded in excess of the latter, and in the analyzed solution iodine and iodine chloride were present together. Their quantities were determined by difference of two titrations of one and the same iodine solution, before and after introducing chlorine. Since each iodine molecule during titration used twice as much sodium thiosulfate as for 1 atom of free iodine, the increase in volume of $\text{Na}_2\text{S}_2\text{O}_3$ solution therefore, was recalculated to the number of gram atoms of iodine corresponding to the number of moles of iodine chloride formed. The solution was analyzed immediately after termination of the experiment by means of three parallel determinations. Samples of the solution were taken by pipette (with three-way stopcock, 25 ml volume) directly from the calorimetric beaker while still closed — through an outlet in the calorimeter. The solution in the pipette was poured into a flask with potassium iodide dissolved in 25 ml of water. Since the flasks with KI had been weighed beforehand, after a second weighing, the solution was analyzed, and sample weights determined. Because of the fact that the iodine solution was taken in weight units and not volume units for the experiment, as the final weight of sample analyzed there was taken the weight after deducting the chlorine which was passed into the sample and reacted. After weighing, the solution was immediately diluted with water and titrated with sodium thiosulfate solution.

Calculation of the thermal effect for the reaction, on the basis of data obtained, was carried out (Table 2) in a manner similar to that which was carried out in determination of the heat of interaction of lead tetrachloride with iodine:

$$\Delta H_{293}^0 = \frac{Q \cdot \Delta \theta}{\Delta T \cdot n} = \frac{Q \cdot \Delta \theta \cdot 1000}{\Delta T \cdot B \cdot \frac{V_2 V_1}{b_1 - a} N}$$

6. Heat of Formation of Lead Tetrachloride from Crystalline Lead Chloride and Gaseous Chlorine

From the reaction cycle given above, it follows that the heat of formation of lead tetrachloride from crystalline lead chloride and gaseous chlorine (ΔH^0) is: $\Delta H^0 = 2\Delta H_2^0 - \Delta H_1^0$, where ΔH_2^0 is equal to the heat of formation of one mole of iodine chloride and ΔH_1^0 is equal to the heat of interaction of one mole of lead tetrachloride with iodine.

Replacing ΔH_2^0 and ΔH_1^0 values we find that

$$\Delta H^0 = 2.6395 + 19793 = +7003 \text{ cal/mole}$$

Taking into account the average absolute and maximum absolute error, the final outcome is

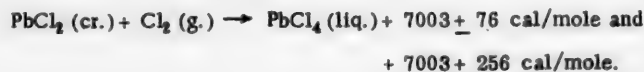


TABLE 2

Heat of Formation of Iodine Chloride from Gaseous Chlorine and Iodine Dissolved in Carbon Tetrachloride

Index	Symbol	Experiment No.			
		1	2	3	4
Weight of iodine solution	B	498.40	498.40	498.35	498.48
Results of analysis	$\frac{V_1}{a}$	0.6051	0.6051	0.6051	0.6073
	$\frac{V_2}{b_1}$	1.0179	1.0115	1.0193	1.0205
	$\frac{V_2}{b_1} - \frac{V_1}{a}$	0.4128	0.4064	0.4142	0.4132
Normality of sodium thiosulfate solution. . .	N	0.09773	0.09773	0.09773	0.09773
Temperature rise.	$\Delta\theta$	1.093	1.068	1.100	1.091
Correction for radiation during reaction . . .	$\Delta(\Delta\theta)$	+ 0.0003	+ 0.0110	+ 0.0080	+ 0.0040
Temperature rise.	ΔT	0.996	1.026	0.963	1.001
Correction for radiation during passage of electric current through spiral	$\Delta(\Delta T)$	+ 0.028	+ 0.031	+ 0.032	+ 0.026
Amperage	I	2.7651	2.7568	2.7199	2.7508
Voltage.	E	2.7820	2.7730	2.7400	2.7680
Duration of current passage (in seconds) . . .	t''	64.4	66.4	64.0	65.4
Quantity of heat (in cal.) evolved during reaction.	Q	117.32	120.43	112.96	117.94
Thermal effect of reaction	ΔH_{298}^0	-6403	-6333	-6396	-6386
Average value for thermal effect	ΔH_{298}^0	-(6403 + 6396 + 6386) : 3 = 6395 cal/mole			
Average absolute error	$\Delta(\Delta H_{298}^0)$	+ 6 cal/mole			
Average relative error	-	0.1%			

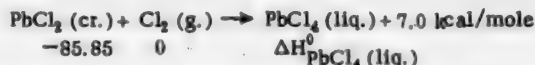
TABLE 3

Heat of Dissolution of Lead Tetrachloride in Carbon Tetrachloride

Index	Symbol	Experiment No.			
		1	2	3	4
Weight of CCl_4 taken for the experiment	B	493.63	493.98	494.28	494.18
Weight of sample analyzed	b	39.96	39.95	39.98	39.85
Weight of PbSO_4 separate sample	a	0.8685	0.7597	0.7411	0.5480
Weight of PbCl_2 separate sample	c	0.9996	0.8744	0.8530	0.6307
Weight of CCl_4 separate sample.	(b-c)	38.960	39.076	39.127	39.230
Concentration of solution	$\frac{\text{PbCl}_2}{\text{CCl}_4}$	$\frac{1}{1121}$	$\frac{1}{1282}$	$\frac{1}{1315}$	$\frac{1}{1778}$
	$\Delta\theta$	-0.215	-0.191	-0.190	-0.127
Temperature drop	$\Delta(\Delta\theta)$	-0.002	+ 0.001	0.000	+ 0.001
Correction for radiation during dissolution. . . .	ΔT	0.293	0.256	0.305	0.349
Temperature rise.	$\Delta(\Delta T)$	+ 0.008	+ 0.009	+ 0.012	+ 0.015
Correction of radiation during passage of electric current through spiral	I	2.8235	2.7170	2.680	2.665
Amperage	E	2.810	2.722	2.683	2.676
Voltage.	t''	18.4	17.0	21.0	24.6
Duration of current flow (in seconds)	ΔH_m	699.2	701.5	718.3	664.2
Thermal effect of dissolution (in cal.)	ΔH_m	(699.2 + 701.5 + 718.3) : 3 = 706.7			
Average value	-	+ 8.1 cal/mole			
Average absolute error	-				

7. Standard Heat of Formation of PbCl_4 (liq.) from Elementary Substances

From the literature available [6], the standard heat of formation for PbCl_2 (cryst.) is equal to -85.85 kcal/mole. Using these data, the standard heat of formation is found.



According to the law of Hess $\Delta H_f^\circ \text{PbCl}_4 \text{ (liq.)} = 7.0 - 85.85 = -78.85$ kcal/mole. Consequently:



8. Heat of Dissolution of Lead Tetrachloride in Carbon Tetrachloride

In order to study the nature of lead tetrachloride, and its behavior in carbon tetrachloride its heat of dissolution in the solvent indicated was carried out.

So far as procedure for measurements are concerned, the method for introducing carbon tetrachloride into the calorimeter and the course of analysis, these were carried out essentially as was done in determination of the heat of interaction for lead tetrachloride with iodine. It was necessary, however, to shorten to a considerable degree the duration of the experiment, since lead tetrachloride when dissolved in carbon tetrachloride decomposes on prolonged standing in the calorimeter. Because of this fact, following the final period corresponding to dissolution of PbCl_4 , the author, rather than cooling as was done in the preceding experiments, passed an electric current through the solution. Thus, the final stage of the experiment, during dissolution of PbCl_4 , was at the same time the initial period of the experiment during passage of the electric current.

The first part of the experiment by such a method proceeded normally, and the end of the main experiment corresponded within the limits of accuracy of measurement to a standard temperature of 25°C . However, during the course of the second part of the experiment, a known error was introduced: the average temperature rise during passage of the electric current did not correspond to 25°C , but was approximately 0.1° higher. However, from the quantitative side the error had no important influence since, due to a small rise in temperature with fluctuations of about 0.2° , the deviation in average temperature rise from 25° amounted to about 0.1° , and with a small temperature coefficient for dissolution in CCl_4 the results of measurement could not be greatly affected.

The amount of lead tetrachloride introduced into the calorimeter was as follows: the above-described funnel by means of which the PbCl_4 was introduced into the calorimeter, was moistened beforehand with concentrated sulfuric acid. Without this seemingly insignificant operation, the experiments would not be successful. Very strong turbidity in the solution was noted in the beaker, as well as the formation of PbSO_4 precipitate. This once again gave evidence of the extreme sensitivity of lead tetrachloride to moisture.

The quantity of lead tetrachloride introduced into the calorimeter was determined by analysis of the solution after the experiment. For such purpose, a sample removed from the calorimeter was introduced into the carbon tetrachloride solution of iodine. The amount of lead chloride formed in this case was then determined by the usual gravimetric procedure according to the sulfate method.

The thermal effect of dissolution for (ΔH_m) per mole of PbCl_4 was found from the equation

$$\Delta H_m = \frac{0.23891 \cdot E \cdot t'' \cdot 0.9913 \cdot \Delta \theta \cdot 349.05}{\Delta T \cdot A} \text{ cal.}$$

or after replacing A by its corresponding values:

$$\Delta H_m = \frac{0.23891 \cdot E \cdot t'' \cdot 0.9913 \cdot \Delta \theta (b-c) 303.28}{\Delta T \cdot B \cdot a} \text{ cal.}$$

All data for thermochemical measurements are given in Table 3.

Although in the first three experiments the extent of dissolution increased with dilution, in the fourth experiment, when dilution was greatest, it reached its lowest value. This can be explained either by a lower accuracy of measurements or by some peculiarity in the course of the curve in the range of the highest dilutions.

* A = weight of PbCl_4 taken for experiment.

Since a study of this problem was not contemplated by the author, it was therefore decided to reject the results of the last experiment.

The result obtained is in agreement with the natures of both substance and solvent. In fact, the symmetry of the CCl_4 molecule (dipole moment equal to zero) and the slight polarity of the PbCl_4 molecule exclude possibility for formation of any compounds in the solution with any marked change in reserve energy. It can also be postulated that during dissolution there occurs a disrupting process of weakly-associated lead tetrachloride molecules, accompanied by negligible energy absorption.

Taking into account the average absolute error, the thermal effect of lead tetrachloride dissolution in carbon tetrachloride consists of $+706.7 \pm 8.1$ cal/mole.

Because of the extremely low stability of lead tetrachloride, the authors did not carry out all of the measurements of thermal effects in formation of the more concentrated solutions. Even at relatively low concentrations with which the author dealt, some turbidity was noted in the solutions while taking the measurements.

SUMMARY

1. Heats of the following reactions under standard conditions have been measured:



The first reaction has been found to be exothermic and equal to -19793 ± 64 cal.; the second reaction has been found to be exothermic and equal to -6395 ± 6 cal.

2. From the data obtained, the heat of formation of lead tetrachloride from crystalline lead chloride and gaseous chlorine has been found. The effect of the reaction has been found to be endothermic, and equal to $+7003 \pm 76$ cal. i.e.,



3. From data obtained, and from literature data by calculation, it has been found that the standard heat of formation of $\text{PbCl}_4 (\text{liq.})$ from elementary substances is equal to 78.85 kcal/mole, i.e.,



4. The thermal effect of lead tetrachloride dissolution in carbon tetrachloride has been measured under standard conditions. The thermal effect has been found to be endothermic, and equal to $+706.7 \pm 8.1$ cal.

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MOLECULAR COMPOUNDS OF ALUMINUM BROMIDE WITH NITROBENZENE IN ETHYLENE BROMIDE SOLVENT

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An investigation of highly concentrated electrolyte solutions has demonstrated that the law of decrease in molar electroconductivity corrected for viscosity with respect to dilution is followed by all highly-concentrated electrolyte solutions [1]. It has been demonstrated at the same time that the isotherms $\mu \cdot \eta - \varphi$ ($\mu \cdot \eta$ = product of molecular conductivity times viscosity, and φ equals dilution) are either superimposed upon one another, or are close together [2]. An investigation of the relationship between molar electroconductivity corrected for viscosity and dilution at various temperatures for a number of aluminum bromide complex compounds in nitrobenzene as the solvent have indicated that the isotherms $\mu_1 - \varphi$ (μ_1 equals molar electroconductivity corrected for viscosity) are not superimposed upon one another, but differ considerably among themselves [3]. This phenomenon is explained by the fact that instead of one, there are in fact two and more electrolytes in the solution, i.e., the system is not a binary one [4].

However, in calculating the molar electroconductivity, the author proceeded on the basis of one electrolyte dissolved, and the fact that new electrolytes may be formed as a result of interaction was not taken into account, for example.



although both of these complexes conduct the current. Naturally, under such conditions electroconductivity isotherms would not be expected to superimpose upon one another.

Thus, on the basis of molecular electroconductivity isotherms, corrected for viscosity, it can be considered that one or more electrolytes are formed in the system.

Insofar as the molecular electroconductivity isotherms for complexes of aluminum halides with nitrobenzene do not superimpose, it can then be considered that the systems: $\text{SbBr}_3 \cdot \text{AlBr}_3 - \text{C}_6\text{H}_5\text{NO}_2$, $\text{NaCl} \cdot \text{Al}_2\text{Br}_6 - \text{C}_6\text{H}_5\text{NO}_2$, $\text{NaBr} \cdot \text{Al}_2\text{Br}_6 - \text{C}_6\text{H}_5\text{NO}_2$, $\text{KBr} \cdot \text{Al}_2\text{Br}_6 - \text{C}_6\text{H}_5\text{NO}_2$, $\text{NH}_4\text{Br} \cdot \text{Al}_2\text{Br}_6 - \text{C}_6\text{H}_5\text{NO}_2$ [3], are not binary, i.e., as a result of interaction of solvent with aluminum bromide, there are formed several electrolytes. Such assumption is justified by the fact that nitrobenzene forms several complex compounds with aluminum halides. Thus, for example, with nitrobenzene, aluminum chloride forms the compounds $\text{AlCl}_3 \cdot 2\text{C}_6\text{H}_5\text{NO}_2$, $\text{AlCl}_3 \cdot \text{C}_6\text{H}_5\text{NO}_2$ [5] and $\text{Al}_2\text{Cl}_6 \cdot \text{C}_6\text{H}_5\text{NO}_2$ [6]. Aluminum bromide produces with nitrobenzene two compounds, $\text{AlBr}_3 \cdot \text{C}_6\text{H}_5\text{NO}_2$ [7] and $\text{AlBr}_3 \cdot 2\text{C}_6\text{H}_5\text{NO}_2$ [8]. However, by the method of thermal analysis, only one compound, $\text{AlBr}_3 \cdot \text{C}_6\text{H}_5\text{NO}_2$ [7] was found. A compound of the same composition was determined by Klochko [9], who studied the electroconductivity, viscosity and specific gravity for the binary system $\text{AlBr}_3 - \text{C}_6\text{H}_5\text{NO}_2$ over the entire range of concentrations.

From $\mu_1 - \varphi$ isotherms for the systems consisting of AlBr_3 complexes with halides of the Groups I and V elements of the periodic system and nitrobenzene as the solvent, it follows that there should be more than one electrolyte in the solution, the author resolving therefore, to study the interaction of AlBr_3 with $\text{C}_6\text{H}_5\text{NO}_2$ in ethylene bromide as the solvent for two isomolar concentrations and at various temperatures. For this purpose the following properties were studied: viscosity, electroconductivity and specific gravity over the entire range of concentrations; the total moles of $\text{AlBr}_3 + \text{C}_6\text{H}_5\text{NO}_2$ remaining constant at all times per one mole of solvent ($\text{C}_2\text{H}_4\text{Br}_2$).

Speaking of a complete range of concentrations, the author had in mind those components whose interactions have been studied in the given case (AlBr_3 and $\text{C}_6\text{H}_5\text{NO}_2$).

Ethylene bromide in this system was considered as the medium, which made it possible to carry out the investigation at relatively low temperature, and to work with substances of limited solubility. This was justified by another fact, that ethylene bromide does not form complexes with aluminum bromide [10]. Thus, investigations of such a type, it would seem, meet the demands of physico-chemical analytical principles.

TABLE 1

Mole ratio $\frac{\text{AlBr}_3 + \text{C}_6\text{H}_5\text{NO}_2}{\text{C}_2\text{H}_4\text{Br}_2} = 0.05$. Temperature 20°

AlBr ₃ (mol. %)	d_4^{20}	$\eta \cdot 10^2$	AlBr ₃ (mol. %)	d_4^{20}	$\eta \cdot 10^2$
100	2.2352	1.999	38.01	2.1631	1.985
71.81	2.1951	2.052	12.62	2.1380	1.878
62.56	2.1858	2.054	0	2.1248	1.819
50.05	2.1738	2.021			

Starting Substances and Working Procedure

Nitrobenzene was purified according to Bruner [11], dried over fused calcium chloride, then distilled, dried over P_2O_5 , and finally distilled into tapered test tubes, which were sealed immediately after filling. Samples distilling at one point were taken for the work. The aluminum bromide was prepared from aluminum shavings and bromine, and was kept in the same manner as described in preceding articles [2]. After thorough purification, the ethylene bromide was frozen out, dried over fused calcium chloride, distilled, dried a second time, and then distilled into test tubes which were sealed.

Electroconductivity was measured with a vacuum tube oscillator with optical indicator, diagram of which is shown in reference [12]. Measurements were taken to avoid traces of moisture in the work [13]. Thermostatic temperature was maintained with an accuracy of $\pm 0.1^\circ$.

Electroconductivity, Viscosity and Specific Gravities

$\text{AlBr}_3\text{--C}_6\text{H}_5\text{NO}_2$ has been investigated many times, but due to the limited solubility of AlBr_3 in $\text{C}_6\text{H}_5\text{NO}_2$ at room temperature, it was not possible to follow changes in any one property over a complete range of concentrations of components.

It was established during investigation of electroconductivity for the indicated system that with an increase in concentration of AlBr_3 the specific electroconductivity forms one maximum [14]. Investigation of the same system over the complete range of concentrations of components at a temperature of 100° made it possible to distinguish 2 maxima and 1 minimum, corresponding to an equimolecular composition of the compound. Other properties of this system which were studied pointed to the same composition for the complex [9].

The interaction of AlBr_3 with $\text{C}_6\text{H}_5\text{NO}_2$ was studied at two isomolar concentrations, of 0.05 and 0.15, in ethylene bromide as solvent, carried out at 20°, 25° and 30°.

A study of the interaction between two components in an indifferent medium made it possible to observe a change of one or the other property within the entire range of concentrations because the 2 components were changing, and the third—the solvent—was constant; a study was carried out, starting with the binary system, for example A—B, and again with the ternary system, A—B—C, and again with the binary system B—C, with constant mole ratio of components.

To avoid overburdening the paper with extensive numerical data, only data for 20° are given. The remaining results of measurements are presented graphically in Figs. 1 and 2.

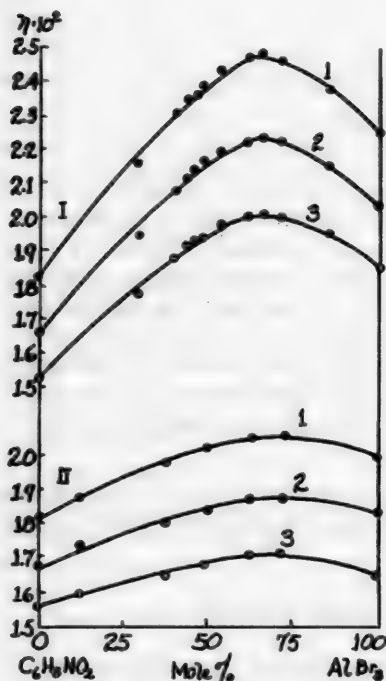


Fig. 1. Relation of viscosity isotherms for a ternary system to composition for two isomolar concentrations: I) 0.15 and II) 0.05. 1) 20°; 2) 25°; 3) 30°.

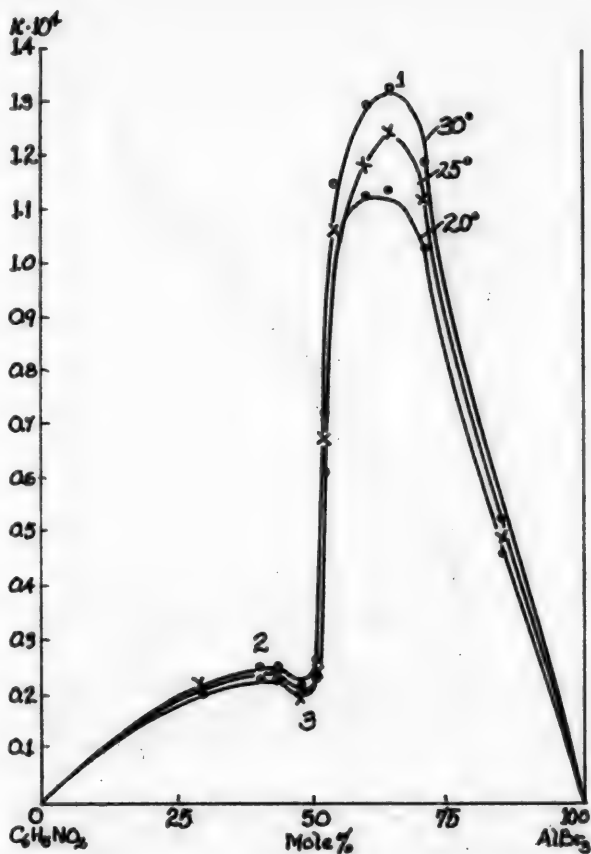


Fig. 2. Dependence of specific electroconductivity isotherms for a ternary system on composition at isomolar concentration of 0.15. 1) $\text{Al}_2\text{Br}_6 \cdot \text{C}_6\text{H}_5\text{NO}_2$; 2) $\text{AlBr}_3 \cdot 2\text{C}_6\text{H}_5\text{NO}_2$; 3) $\text{AlBr}_3 \cdot \text{C}_6\text{H}_5\text{NO}_2$.

The curves in Fig. 2 indicate a relationship of specific electroconductivity to the concentration of components in the system for an isomolar concentration $\text{AlBr}_3 + \text{C}_6\text{H}_5\text{NO}_2$ equal to 0.15. With an increase in AlBr_3 concentration, the specific electroconductivity increases, then decreases a little, forming a gentle maximum, and on further increase in concentration increases sharply, passing through a maximum and falling quite rapidly. The character of the curves remains the same, i.e., both maximum and minimum are preserved upon introducing a correction for viscosity. Thus, from the isotherms of specific electroconductivity it can be postulated that three compounds are formed in the solution: $\text{AlBr}_3 \cdot 2\text{C}_6\text{H}_5\text{NO}_2$, $\text{AlBr}_3 \cdot \text{C}_6\text{H}_5\text{NO}_2$ and $\text{Al}_2\text{Br}_6 \cdot \text{C}_6\text{H}_5\text{NO}_2$; the latter compound is found to be more conductive. It is characteristic that the viscosity maximum coincides with the maximum for the specific electroconductivity corresponding to a composition of the complex with the highest electrical conductivity. With an increase in temperature, the electroconductivity increases somewhat, the product $\kappa \cdot \eta$ decreasing.

For a comparison of results obtained by the author for conductivity of the ternary system with the data obtained by Klochko [9] for the binary system $\text{AlBr}_3 - \text{C}_6\text{H}_5\text{NO}_2$, the author has introduced a correction for viscosity Klochko's data for specific electroconductivity at 75° and at 100°. Results are given in Fig. 3.

TABLE 2

Temperature 20°

$\text{AlBr}_3 + \text{C}_6\text{H}_5\text{NO}_2$ $\text{C}_6\text{H}_5\text{Br}_2$	AlBr_3 (mol. %)	d_4^{20}	$\eta \cdot 10^2$	$\kappa \cdot 10^4$
0.1500	100	2.2835	2.248	—
0.1501	85.37	2.2494	2.384	0.453
0.1500	71.52	2.2142	2.462	1.028
0.1497	65.70	2.2020	2.484	1.134
0.1496	61.46	2.1926	2.470	1.121
0.1499	55.60	2.1770	2.451*	0.981
0.1496	53.50	2.1696	2.439	0.609
0.1498	51.78	2.1680*	2.424	0.219
0.1501	48.65	2.1585	2.391	0.189
0.1501	46.16	2.1520*	2.362	0.218
0.1596	44.04	2.1459	2.357	0.219
0.1499	40.47	2.1374	2.311	0.224
0.1499	29.73	2.1070	2.156	0.212
0.1504	0	2.0293	1.817	—

* Found by interpolation.

The relationship between viscosity of the system to ratio of $\text{AlBr}_3 + \text{C}_6\text{H}_5\text{NO}_2$ components, whose mole sum is taken as 100%, is presented in Fig. 1. The isotherms show results of measurement at two isomolar concentrations, 0.05 and 0.15.

It can be seen from the curves given that temperature increase and dilution lead to a decreased viscosity for the system, while the maximum gradually loses its depth.

Numerical values for viscosity plotted directly on the ordinates axis correspond to viscosity for the binary systems $\text{AlBr}_3 - \text{C}_2\text{H}_5\text{Br}_2$ and $\text{C}_6\text{H}_5\text{NO}_2 - \text{C}_2\text{H}_5\text{Br}_2$. The viscosity maximum resulting at these concentrations indicates formation in the solution of a compound having the composition $\text{Al}_2\text{Br}_6 \cdot \text{C}_6\text{H}_5\text{NO}_2$.

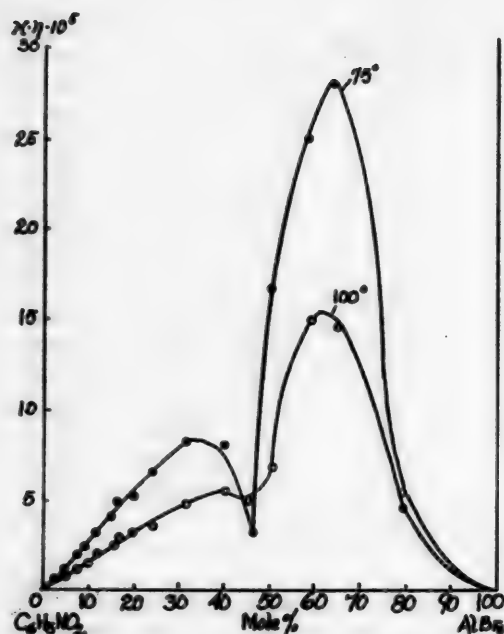


Fig. 3. Relationship of specific electroconductivity, corrected for viscosity of the AlBr_3 - $\text{C}_6\text{H}_5\text{NO}_2$ binary system to composition at 75° and 100°, according to the data of Klochko [9].

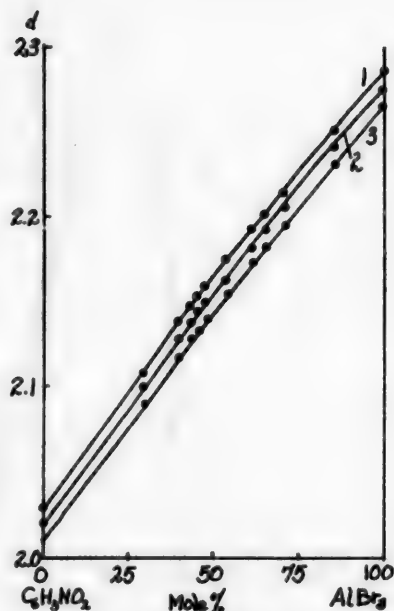


Fig. 4. Relation of specific gravity for the ternary system to the composition at isomolar concentration of 0.15. 1) 20°; 2) 25°; 3) 30°.

As can be seen from Fig. 3, the specific electroconductivity corrected for viscosity upon increased concentration of AlBr_3 forms two maxima and 1 minimum, which one author's data also indicate, for formation of three complex compounds, to which the author [9] paid no attention.

A certain shift of the minimum in the direction of lower AlBr_3 concentration is caused by difficulties in the experiment at the indicated temperatures for such compounds as AlBr_3 and $\text{C}_6\text{H}_5\text{NO}_2$.

The Fig. 4 isotherms characterize the relationship of specific gravity for the system to the ratio of components at isomolar concentration of AlBr_3 + $\text{C}_6\text{H}_5\text{NO}_2$ equal to 0.15. The bend on the isotherms, resulting from intersection of two straight lines, corresponds to compositions for the $\text{AlBr}_3 \cdot \text{C}_6\text{H}_5\text{NO}_2$ compound.

EVALUATION OF RESULTS

Analysis of the data obtained has indicated that, like AlCl_3 , aluminum bromide with nitrobenzene forms 3 complex compounds which are apparently less stable, and therefore, were not characterized.

The fact that thermal analysis discloses only one compound is perhaps explained by the fact that the concentration region in which $\text{Al}_2\text{Br}_6 \cdot \text{C}_6\text{H}_5\text{NO}_2$ compound predominates possesses a higher viscosity, which inhibits crystallization. It is also known that nitrobenzene solutions possess the property of being considerably supercooled. In addition, the existence of explosions at high temperatures in the region of high AlBr_3 concentrations makes the experiment difficult.

The procedure used by the author for a study of the interaction between two components in a third component, providing it is inert to the other two, makes it possible to circumvent a number of difficulties which appear during the investigation of ternary systems (limited solubility under normal conditions, high temperature, decomposition of reactants, and others) and is in complete agreement with principles of physico-chemical analysis. A theoretical substantiation of this procedure is analyzed in detail by Izmailov [15].

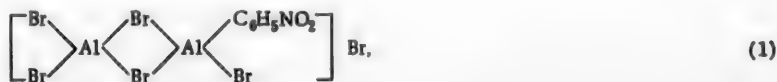
It can be seen from the data given that for the systems in which two components form several compounds, the system's viscosity is primarily, due to that compound which has the greatest viscosity in solution, and the best

electrical conductivity. Moreover, during crystallizations of similar systems, it has been observed that the least dissociated and least electrical-conductive compound is the first to crystallize.

Thus, it follows from the author's investigations that aluminum bromide with nitrobenzene forms 3 compounds according to the electroconductivity data: $\text{AlBr}_3 \cdot 2\text{C}_6\text{H}_5\text{NO}_2$, $\text{AlBr}_3 \cdot \text{C}_6\text{H}_5\text{NO}_2$ and $\text{Al}_2\text{Br}_6 \cdot \text{C}_6\text{H}_5\text{NO}_2$, which, according to the conductivity values, are arranged in the following descending order:



Such an order for conductivity values is in accord with possible structural schemes for these complex compounds, proceeding from a coordination number of four for aluminum:



A compound of equimolecular composition is expressed by the formula $\text{Al}_2\text{Br}_6 \cdot 2\text{C}_6\text{H}_5\text{NO}_2$, in which complex aluminum possesses a coordination number of 4 [16].

Of the compounds given, the least stable is $\text{AlBr}_3 \cdot 2\text{C}_6\text{H}_5\text{NO}_2$, which follows from the negative temperature coefficients of conductivity [9] over a concentration range with a predominance of this compound, and the character of the first maximum (Figs. 2 and 3).

Structural schemes given for aluminum bromide complex compounds with nitrobenzene are in full accord with the data according to transference numbers for the $\text{AlBr}_3\text{--C}_6\text{H}_5\text{NO}_2$ system.

Sheka and Pechenaya [17] have studied the transference numbers for the system $\text{AlBr}_3\text{--C}_6\text{H}_5\text{NO}_2$ within the concentration range of 2-28 weight % and have demonstrated that with increase in AlBr_3 concentration, the numerical values for transference numbers changed. This indicates without doubt that the system is not binary, and that in the solution are, as the authors point out, several complex ions. The change in concentration of AlBr_3 shifts the equilibrium between the complex compounds formed in solution and leads to predominance of one over the others, because of which a constancy in transference numbers cannot be observed.

The authors have demonstrated that during electrolysis the AlBr_3 concentration in the anode area increases and bromide ion concentration predominates, i.e., for a transference number equal to 0.73 for $\frac{1}{3} \text{Al}^{+++}$, the corresponding transference number for bromide is 1.85, and for an aluminum transference number of 1.1, the bromide transference number is equal to 2.05. These data, it would seem, give grounds for assuming that in solution with AlBr_4^- anion, there also exist free Br^- ions, which confirms the above-given structural schemes for the complex compounds forming during interaction of AlBr_3 with $\text{C}_6\text{H}_5\text{NO}_2$.

The results examined confirm without question the author's assumptions concerning the cause for the fact that isotherms of molecular electroconductivity corrected for viscosity for complex compounds of aluminum halides in nitrobenzene do not superimpose on one another, as was observed for other systems, which is apparently related to an interaction of nitrobenzene with aluminum halides.

Upon studying the system $\text{AlBr}_3\text{--SbBr}_3\text{--C}_6\text{H}_5\text{NO}_2$ by viscosity and electroconductivity, it has been demonstrated that the compound $\text{AlBr}_3 \cdot \text{C}_6\text{H}_5\text{NO}_2$ is more stable than the compound $\text{SbBr}_3 \cdot \text{AlBr}_3$ [18].

During dissolution of aluminum halide complexes of the type $\text{MeHal} \cdot \text{Al}_2\text{Br}_6$ in nitrobenzene, the latter apparently removes an aluminum bromide molecule from these compounds, with which it enters into reaction and forms new compounds. This also follows from the fact that alkali metal halides are not displaced by nitrobenzene from compounds with AlBr_3 , since otherwise, because of their insolubility in $\text{C}_6\text{H}_5\text{NO}_2$, they would have precipitated out, which was not observed.

Thus, by a study of the isotherms of molecular electroconductivity corrected for viscosity, in solution for one or more electrolytes, a qualitative estimation can be made concerning the formation in solution of one or more electrolytes, because in this case the electroconductivity isotherms corrected for viscosity do not superimpose on one another.

SUMMARY

1. Viscosity, electroconductivity and specific gravities for the system $\text{AlBr}_3\text{--C}_6\text{H}_5\text{NO}_2\text{--C}_2\text{H}_4\text{Br}_2$ with two isomolar concentrations, and at temperatures of 20°, 25° and 30° have been studied.

2. According to the electroconductivity data, AlBr_3 forms with $\text{C}_6\text{H}_5\text{NO}_2$ three compounds: $\text{AlBr}_3 \cdot 2\text{C}_6\text{H}_5\text{NO}_2$, $\text{AlBr}_3 \cdot \text{C}_6\text{H}_5\text{NO}_2$ and $\text{Al}_2\text{Br}_6 \cdot \text{C}_6\text{H}_5\text{NO}_2$. According to viscosity data, one compound, $\text{Al}_2\text{Br}_6 \cdot \text{C}_6\text{H}_5\text{NO}_2$, and according to specific gravity data $\text{AlBr}_3 \cdot \text{C}_6\text{H}_5\text{NO}_2$, are formed.

3. It has been demonstrated that the cause of the fact that electroconductivity isotherms, corrected for viscosity, for aluminum halide complexes in nitrobenzene do not superimpose on one another is due to interaction of components of the system with the formation of more than one electrolyte in solution.

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HETEROTRIACIDS

IV. SYNTHESIS AND ANALYSIS OF GERMANIUMTUNGSTOVANADIC ACID

A. I. Kokorin and N. A. Polotebnova

In synthesizing 1-vanadium-10-tungstogermanic acid, Ivanov-Emin [1] used germanium dioxide, ammonium paratungstate and ammonium vanadate. The ammonium vanadate used during synthesis was taken in larger amounts than would be required according to the stoichiometric calculations. The authors have not succeeded in reproducing the synthesis according to the above-indicated directions. In a majority of the cases, during acidification of a solution of the mixture of starting materials with 30% sulfuric acid to a definitely acid reaction, there precipitated out vanadium anhydride. Subsequent addition of acid in order to obtain the etherate caused formation of a yellow tungstic acid precipitate, and the etherate failed to separate. This fact is explainable, in all probability, by the fact that the authors attempted reproduction of the synthesis using considerably smaller quantities of starting materials. To carry out experiments with large amounts of starting material, however, was, to the authors, inexpedient, first because of the need to economize on germanium, and second, formation of tungsten acid precipitate would be unavoidable in any case.

Investigations completed by the authors on the synthesis of saturated germanium-molybdenumvanadic acid [2] have indicated that during the formation of the given heterotriacid, temperature control is a decisive factor, as well as the quantitative ratio of starting materials taken for the synthesis. It was natural to assume that these factors would have an effect during preparation of germaniumtungstovanadic acid, since heterotriacids containing tungsten are synthesized with greater difficulty than their molybdenum analogs [3]. On the other hand, during preparation of silico tungstovanadic acid by the etherate method, the authors established that the use of sodium paratungstate as starting material does not lead to production of the saturated heterotriacid. The problem in question is successfully solved if metatungstate is used for the synthesis [4].

Proceeding from the indicated concept, and from the fact that germanium is found to be like the silicon analog, the authors decided to develop a new method for synthesis of germaniumtungstovanadic acid. After a number of trials, the authors succeeded in solving this problem.

EXPERIMENTAL

Synthesis. Metallic germanium, normal sodium tungstate and sodium metavanadate were taken as the starting materials.

Metallic germanium was first converted to a solution by treating it with hydrogen peroxide, and by subsequent dissolution of the resulting germanium dioxide in alkali (NaOH). The normal sodium tungstate was converted into the metatungstate by addition of tungstic acid to a boiling solution of the sodium tungstate, weights taken of which were in the ratio of 1:1. A small amount of tungstic acid which did not react was filtered off [4].

Calculation of the amounts of substances necessary for synthesis of the heterotriacid was computed from the ratio of Ge:W:V as 1:10:2; however, four times as much vanadium was taken as required by stoichiometric calculation.

In separate experiments, the following amounts of materials were involved: Ge—0.05 g, $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ —2.3 g, WO_3 —2.3 g, and NaVO_3 —0.7 g.

Sodium germanate and vanadate solutions were added to a solution of the resulting sodium tungstate placed in a conical flask of 50 ml volume. The volume of liquid at the start of the experiment amounted to approximately 20-25 ml. The flask contents were acidified with several drops of H_2SO_4 (1:1), to the appearance of a bright orange color. 4-5 drops of the acid was used. The solution was boiled for 1.5 hours. During the boiling process,

water was added several times in such a manner that the volume of liquid up to the completion of the experiment was kept equal to 10 ml. 5 ml of H_2SO_4 (1:1) was then added dropwise to the boiling solution, with vigorous stirring. At times, in some experiments, a slight turbidity resulted at the end of the sulfuric acid addition. The liquid was cooled, transferred to a separatory funnel of 50 ml volume, and ether added. Upon gentle shaking, drops of the orange etherate immediately began to form. Another 5 ml of H_2SO_4 (1:1) was added during the process of etherate separation. The solution over the etherate became yellow, and then green. The etherate was left undisturbed for 12-24 hours, then transferred to a low cylindrical vessel, the etherate decomposed with a small amount of water, and left to crystallize. The orange-red crystals which precipitated were filtered through a glass filter under vacuum. Yield of crystals amounted to 85% of theory.

Parallel experiments for preparation of germaniumtungstovanadic acid were arranged, in which twice as much vanadate was taken as required by stoichiometric calculation. In this case a mixture of acids apparently results. The determined amounts of tungsten and vanadium showed a W:V ratio of 10.4:1. Solutions of this acid began to show turbidity after 24 hours, while at the same time, solutions of the acid obtained as earlier were stable for a prolonged length of time.

Analysis. Water content of the heterotriacid obtained was determined by drying a sample (1 g) and roasting further to constant weight at a temperature of about 400° .

Preliminary decomposition of the heterotriacid by boiling with a mixture of sulfuric and phosphoric acids and water, as well as the subsequent determination of tungsten and vanadium, was carried out in a manner analogous to that described earlier in the analysis of silicotungstovanadic acid [4].

Considerable difficulty was encountered during determination of germanium. The generally accepted method for determination of germanium by distillation with hydrobromic acid led to negative results in all experiments carried out by the authors on analysis of a mixture of the germanium and tungsten compounds. No positive results were obtained by distillation with concentrated hydrochloric acid, either. This fact can be explained on the basis that the tungstic acid which precipitates holds tightly to the germanium, thus making complete distillation impossible. Introduction of oxalic acid into the analyzed mixture before distillation to retain tungsten in solution, as well as to effect a preliminary reduction of the tungsten to lower valencies, increased the quantity of germanium distilled off, but the results were not reproducible. The amount of germanium distilled depended upon the rate of tungsten precipitation in proportion to the hydrochloric acid addition.

Brauer and Renner [5] recommend determination of germanium by tannin precipitation after a preliminary separation of tungsten in the form of tungstic acid. As the authors' experiments have demonstrated, with a low germanium content relative to tungsten, germanium in the filtrate does not precipitate with tannin. It is completely adsorbed and held fast by the tungstic acid precipitate.

After carrying out a series of experiments, the authors were able to establish that good results on determination of small quantities of germanium in the presence of considerable amounts of tungsten are obtained if the germanium is distilled off with concentrated hydrochloric acid in the presence of phosphoric acid and perhydrol, and the germanium precipitated from the distillate by means of tannin. The course of the analysis for germanium in germaniumtungstovanadic acid is given below.

Determination of germanium. A batch of the heterotriacid, 0.2-0.3 g was placed in the flask of a distilling apparatus [2] and dissolved in 3-5 ml of water. For retention of tungsten in the solution, with subsequent addition of the hydrochloric acid, 5 ml of H_3PO_4 (d 1.7) was added to the solution. Into the receiver with distillate was introduced 10 ml of HCl (1:1). The solution in the flask was heated, and 41 ml of concentrated HCl added gradually (as used) from a separatory funnel. Before introducing the last portions of hydrochloric acid, 1 ml of perhydrol was added. The hydrogen peroxide promotes the most complete distillation of germanium due to formation of small amounts of chlorine. After addition of all the hydrochloric acid, 20 ml of H_2SO_4 (1:1) was added, and the heating continued to separation of sulfuric acid fumes. 30-35 ml of concentrated ammonia and water was added to the hydrochloride solution from the receiver, transferred to a beaker, calculated so that the acidity remained equal to 0.5-1 N (total volume of solution 200-250 ml). After cooling, 20 ml of a 5% aqueous solution of tannin was introduced into the solution investigated, and the mixture left standing undisturbed up to 12 hours. The resulting light-brown precipitate was filtered off through a glass filter, washed and dried at $100-105^\circ$ to constant weight. The ratio of germanium to tannin in the precipitate was equal to 1:30 [5]; hence, the coefficient, recalculated from the weight of precipitate, of germanium content was equal to 0.0323. In Table 1 are given results of determination of germanium, tungsten and vanadium recalculated to gram-atomic weights, and water content in moles (upon drying to constant weight at 105°).

TABLE 1

Results of Germaniumtungstovanadic Acid Analysis

Sample No.	Weight (g)	Ge		V		W		Ratio of Ge:V:W	H ₂ O	
		g	g-atom.	g	g-atom.	g	g-atom.		g	molecules
1	0.7839	0.0173	0.000238	0.0254	0.00050	0.4519	0.00245	1:2.1:10.2	0.0762	20
2	1.2023	0.0229	0.000315	0.0322	0.000631	0.6230	0.00338	1:2.0:10.7	0.1627	30
3	0.8025	0.0159	0.00021	0.0224	0.00044	0.4193	0.00228	1:2.1:10.7	0.0963	25

TABLE 2

Germanium, Tungsten and Vanadium Contents in the Precipitate After Reaction with o-Hydroxyquinoline

Found (in %)			Calculated (in %)		
Ge	W	V	Ge	W	V
3.30	91.00	4.85	3.65	91.30	5.05

The analytical results give grounds for believing that the given compound is related to the class of saturated heterotriacids, and may be represented by the formula $H_n[Ge(W_2O_7)_5V_2O_6] \cdot nH_2O$, where $n = 20, 25, 30$, on the basis of the Miolati-Rosenheim theory. In the authors' opinion, the amount of water of crystallization depends upon the conditions of crystallization and is not found to be constant. The total water content found by roasting at 400° amounted to 17-18.5%.

Saturated germanium tungstovanadic acid crystallizes readily in the form of orange-red crystals, and can be readily recrystallized from aqueous solutions. This compound is found to be relatively stable, both in solid form and in solutions. While the starting products (tungsten and vanadate) are precipitated by o-hydroxyquinoline only at very low acidity, the heterotriacid obtained is completely precipitated, even at acidities up to 1.3 N HCl.

After reaction with o-hydroxyquinoline, the precipitates were reanalyzed for their germanium, tungsten and vanadium contents. The average value of three determinations is given in Table 2.

Somewhat lower results were obtained for amounts of germanium, tungsten and vanadium, as compared with theory, which can be explained by experimental errors.

SUMMARY

1. A new, more effective procedure for synthesis of saturated germaniumtungstovanadic acid has been developed. Sodium metatungstate, and not ammonium paratungstate, was used as starting material.
2. Conditions for distillation of a small amount of germanium in the form of tetrachlorogermanium in the presence of large amounts of tungsten are specified.
3. It has been determined that precipitation of small amounts of germanium by means of tannin in the presence of large quantities of tungsten, after separation of the latter in the form of tungstic acid, does not produce positive results.
4. The composition of germaniumtungstovanadic acid which was synthesized has been determined, on the basis of which this compound can be represented by the formula $H_n[Ge(W_2O_7)_5V_2O_6] \cdot nH_2O$, where n equals 20, 25 and 30, and depends upon conditions of crystallization.

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DOUBLE DECOMPOSITION IN THE ABSENCE OF SOLVENT

II. THE QUATERNARY RECIPROCAL SYSTEM OF LITHIUM, POTASSIUM CHLORIDES,

SULFATES AND TUNGSTATES

A. G. Bergman, A. I. Kislova and V. I. Posypaiko

Internal Sections Through the Quaternary Reciprocal System, Li, K || Cl, SO₄, WO₄

Three sections through the composition prism described earlier in the literature [1] have confirmed the stability of complex compounds of $\text{Li}_2\text{SO}_4 \cdot \text{K}_2\text{SO}_4$, $\text{Li}_2\text{WO}_4 \cdot \text{K}_2\text{WO}_4$ and their extensive distribution within the quaternary reciprocal system Li, K || Cl, SO₄, WO₄. To establish dimensions for the inner crystallization volumes and their distribution, tetrahedrons for the prism, the compositions and locations of quaternary eutectic points for the system, and to study salt interactions found in the given system, five internal triangular sections through the prism-composition were studied by the visual-polythermal method [2].

EXPERIMENTAL

Stable Diagonal Section of K_2Cl_2 - Li_2WO_4 - Li_2SO_4

The lateral sides (Table 1, Fig. 1) are found to be stable diagonal sections of Li_2WO_4 - K_2Cl_2 and Li_2SO_4 - K_2Cl_2 of the corresponding reciprocal systems Li, K || Cl, WO₄ and Li, K || Cl, SO₄ [3]. Li_2WO_4 - K_2Cl_2 is found to be a simple eutectic system with the eutectic at 532° and 44% K_2Cl_2 , and a polymorphic conversion of lithium tungstate at 660° and 10.5% K_2Cl_2 .

TABLE 1

Stable diagonal				Section	
K_2Cl_2 - Li_2SO_4		K_2Cl_2 - Li_2WO_4		Li_2WO_4 - Li_2SO_4	
% K_2Cl_2	temperature	% K_2Cl_2	temperature	% Li_2SO_4	temperature
0	860°	0	738°	0	738°
5	672	5	698	5	730
10	590	10	664	10	720
15	538	15	648	20	702
25	490	25	618	30	680
30	460	30	592	35	666
32	456	35	572	37.5	660
35	486	40	550	40	656
40	520	42	540	45	648
52	584	45	544	50	636
60	619	50	560	60	614
72	668	60	612	65	600
80	700	70	660	68	596
90	740	80	698	70	614
100	774	90	740	80	690

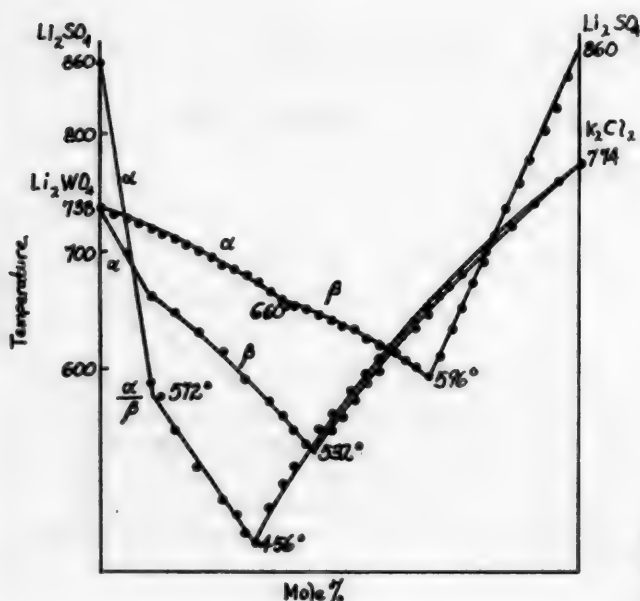


Fig. 1. Lateral sides of the K_2Cl_2 - Li_2WO_4 - Li_2SO_4 section.

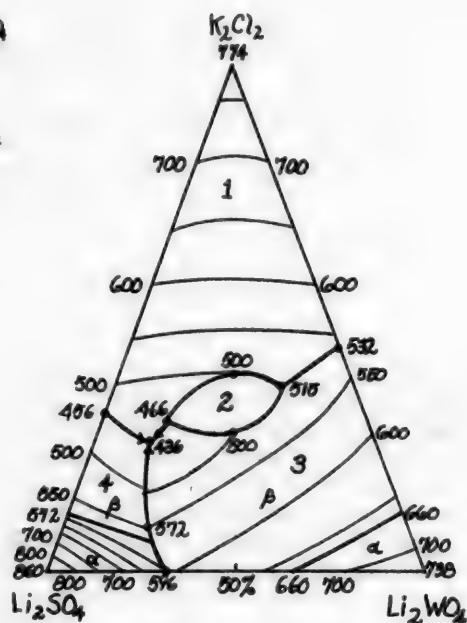


Fig. 2. K_2Cl_2 - Li_2WO_4 - Li_2SO_4 . 1) K_2Cl_2 ; 2) $Li_2SO_4 \cdot K_2SO_4$; 3) β - Li_2WO_4 ; 4) β - Li_2SO_4 .

The melting diagram for Li_2SO_4 - K_2Cl_2 has a more complex character, consisting of three crystallization branches: α - Li_2SO_4 , beginning at 860° and 92.5% Li_2SO_4 , β - Li_2SO_4 at 572° to the eutectic at 456° and 68% Li_2SO_4 , and the K_2Cl_2 branch.

The third lateral side of the triangle for the Li_2WO_4 - Li_2SO_4 profile is found to be the upper base side of the prism. It represents a eutectic system with eutectic at 596° and 68% Li_2SO_4 . The Li_2WO_4 branch is complicated by the polymorphic conversion at 660° and 37.5% Li_2SO_4 .

It was established by means of a number of sections through the triangular composition that the diagram for crystallization surface of K_2Cl_2 - Li_2WO_4 - Li_2SO_4 section consists of six fields of crystallization: α - and β - Li_2SO_4 , K_2Cl_2 , α - and β - Li_2WO_4 , and $Li_2SO_4 \cdot K_2SO_4$ compounds (Fig. 2). The area of $Li_2SO_4 \cdot K_2SO_4$ binary salt separation, which contains K_2SO_4 as an exchange product, is outlined by the heavy line. This area on projection is in the form of a comparatively symmetrical lens, at one end of which is the 515° temperature, and at the other, 466°. This indicates that the crystallization volume for $Li_2SO_4 \cdot K_2SO_4$ complex lies beyond this stable section, but upon lowering of temperature, the complex reacting with lithium salts in liquid form decomposes, converting into a mixture of the three starting components. Consequently, appearance of the complex is found to be temporary, wedging out, and not participating in triangulation of the given triangular section. It can, therefore, be considered for practical purposes as a stable diagonal section for K_2Cl_2 - Li_2WO_4 - Li_2SO_4 with a triple eutectic point at 436° and 25% K_2Cl_2 , 15% Li_2WO_4 and 60% Li_2SO_4 .

Stable non-diagonal profile of K_2Cl_2 -(50% Li_2WO_4 + 50% K_2WO_4)-(50% Li_2SO_4 + 50% K_2SO_4).^{*} Dissection proceeds from a cross section of the lateral reciprocal system, $Li, K || SO_4, WO_4$. Two lateral sides of the triangular composition are found to be stable non-diagonal sections of two squares for the reciprocal systems which are lateral facets of the prism-composition (Table 2, Fig. 3).

1) K_2Cl_2 - D_1 is found to be the stable non-diagonal section of the reciprocal system, $Li, K || Cl, WO_4$, and bears the character of a simple eutectic system with eutectic at 514° and 16% K_2Cl_2 :

2) K_2Cl_2 - D_2 , a stable non-diagonal cross-section of the reciprocal system, $Li, K || Cl, WO_4$, is found to be a eutectic system with eutectic at 585° and 31.5% K_2Cl_2 :

* Provisionary symbol: D_1 equals (50% Li_2WO_4 + 50% K_2WO_4); D_2 equals (50% Li_2SO_4 + 50% K_2SO_4).

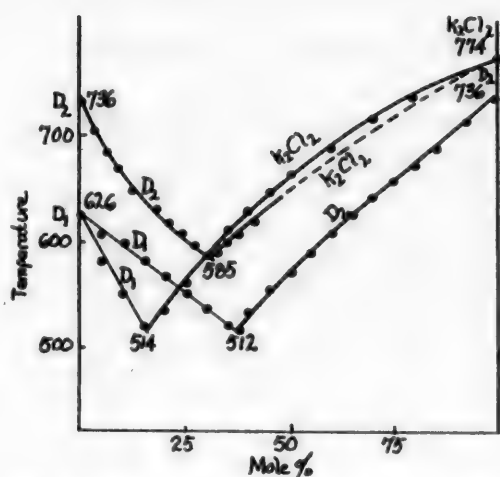


Fig. 3. Lateral sides of the K_2Cl_2 - D_1 - D_2 section.

TABLE 2

Stable non-diagonal				D_1-D_2 section	
$D_2-K_2Cl_2$		$D_1-K_2Cl_2$			
% K_2Cl_2	temperature	% K_2Cl_2	temperature	% D_2	temperature
0	734°	0	628°	0	628°
3	706	5	582	5	608
6	686	10	550	10	598
9	670	15	520	15	580
12	648	20	538	20	568
15	639	25	562	25	550
18	630	30	592	30	536
21	618	35	614	35	520
24	610	40	632	40	532
27	596	50	666	45	554
30	588	60	690	50	572
38	608	70	718	60	610
42	644	80	740	75	656

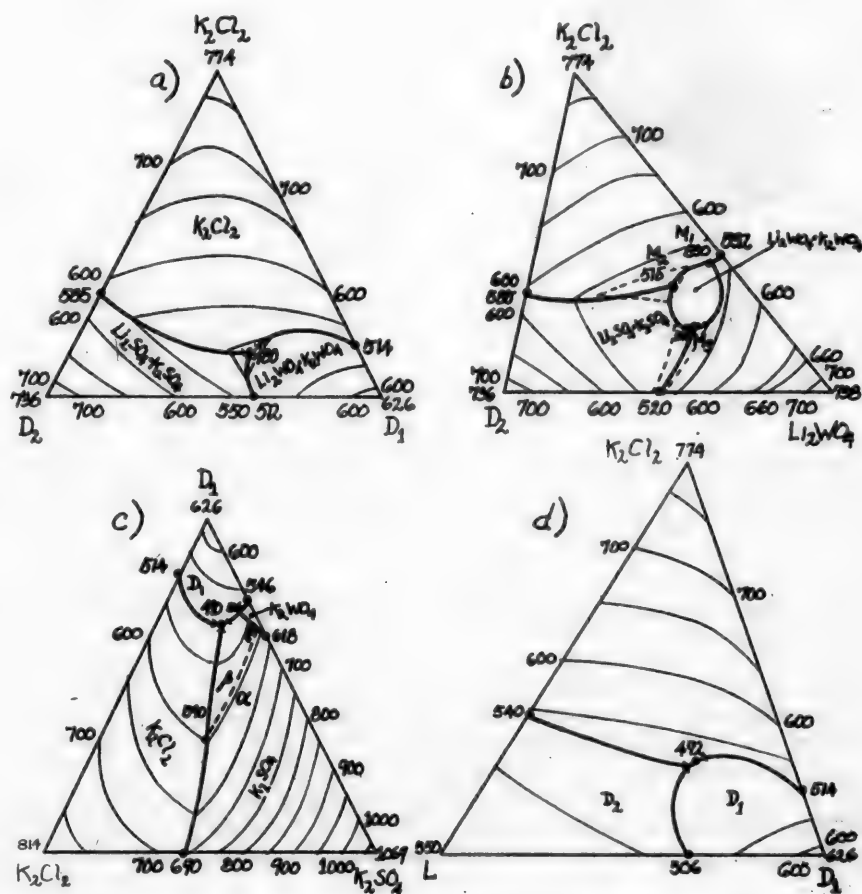


Fig. 4. Sections through $K, Li || SO_4, Cl, WO_4$ system. a) K_2Cl_2 - D_1 - D_2 ; b) K_2Cl_2 - $-Li_2WO_4$ - D_2 ; c) K_2Cl_2 - D_1 - K_2SO_4 ; d) K_2Cl_2 - D_1 - L .

By a number of sections, the character of the crystallization surface for the given section (Fig. 4, a) was established. It consists of three crystallization fields: $\text{Li}_2\text{SO}_4 \cdot \text{K}_2\text{SO}_4$, $\text{Li}_2\text{WO}_4 \cdot \text{K}_2\text{WO}_4$ complex compounds, and K_2Cl_2 .

In the $\text{Li, K} \parallel \text{Cl, SO}_4, \text{WO}_4$ quaternary system, the given section represents a simple triple eutectic system, with eutectic at 480° and a composition: 13% K_2Cl_2 , 55% D_1 , 32% D_2 .

From the given section, the formation of $\text{Li}_2\text{SO}_4 \cdot \text{K}_2\text{SO}_4$ and $\text{Li}_2\text{WO}_4 \cdot \text{K}_2\text{WO}_4$ compounds, melting without decomposition in the quaternary reciprocal system $\text{Li, K} \parallel \text{Cl, SO}_4, \text{WO}_4$ was confirmed and their limits of extension within the prism composition were established.

Additional section of $\text{K}_2\text{Cl}_2 - \text{Li}_2\text{WO}_4 - (50\% \text{Li}_2\text{SO}_4 + 50\% \text{K}_2\text{SO}_4)$. Two lateral sides of the triangular composition for the given section of $\text{Li}_2\text{WO}_4 - \text{K}_2\text{Cl}_2$ binary system and of $\text{K}_2\text{Cl}_2 - \text{D}_2$, are described in two preceding sections. The third lateral side, $\text{Li}_2\text{WO}_4 - \text{D}_2$ is found to be a stable, non-diagonal section of the reciprocal system $\text{Li, K} \parallel \text{SO}_4, \text{WO}_4$ and bears the character of a simple eutectic system with eutectic at 520° and 55% $\text{Li}_2\text{SO}_4 \cdot \text{K}_2\text{SO}_4$.

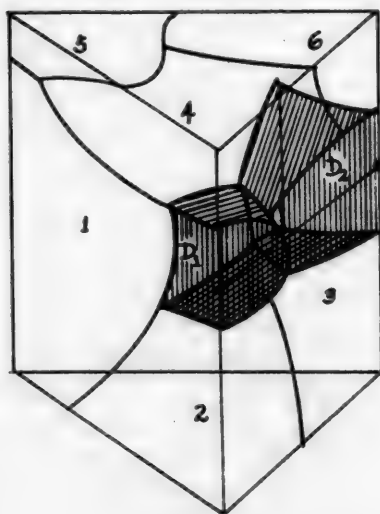


Fig. 5. Inner volumes of the quaternary reciprocal system. 1) K_2Cl_2 ; 2) K_2WO_4 ; 3) K_2SO_4 ; 4) Li_2WO_4 ; 5) Li_2Cl_2 ; 6) Li_2SO_4 . D_1 and D_2 volumes of the complexes.

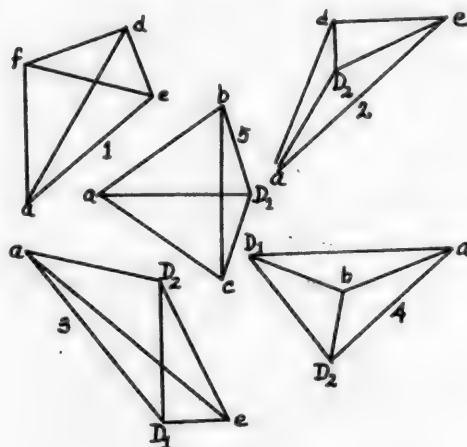


Fig. 6. Tetrahedrons (explanation in text). a) K_2Cl_2 ; b) K_2SO_4 ; c) K_2WO_4 ; d) Li_2SO_4 ; e) Li_2WO_4 ; f) Li_2Cl_2 .

The liquidus curve consists of crystallization branches of the $\text{Li}_2\text{SO}_4 \cdot \text{K}_2\text{SO}_4$ compounds and Li_2WO_4 , with polymorphic conversion at 660° .

In Fig. 4b is given a projection of the diagram for triangle composition section investigated; Isotherms are plotted through each 50° point. This section is somewhat analogous to the $\text{Li}_2\text{WO}_4 - \text{Li}_2\text{SO}_4 - \text{K}_2\text{Cl}_2$ investigated earlier, but is made complicated by the fact that the inner area of the temporarily evolving phase of the $\text{Li}_2\text{WO}_4 \cdot \text{K}_2\text{WO}_4$ complex has a more complex depth. At the boundary lines there are three triple monovariant points: $\text{M}_1 - 530^\circ$; $\text{M}_2 - 515^\circ$ and $\text{M}_3 - 515^\circ$, which, under the conditions of disappearance in crystallization volume of the complex, should merge into one quaternary point. The position of this merging point in the prism should be considered as at approximately a temperature of 500° , and corresponding in content to the II tetrahedron (see below).

The given section dissects the inside of the prism for the crystallization volume of Li_2WO_4 (α - and β - volumes), for K_2Cl_2 , the volume of the compound $\text{Li}_2\text{SO}_4 \cdot \text{K}_2\text{SO}_4$, and the volume of the temporarily evolving phase of the $\text{Li}_2\text{WO}_4 \cdot \text{K}_2\text{WO}_4$ complex.

$K_2Cl_2-D_1-K_2SO_4$ section melting with decomposition. Two lateral sides of the triangular composition are found to be stable non-diagonal sections of two squares for the reciprocal systems, the lateral facets of the prism.

1) $K_2Cl_2-D_1$ was described earlier.

2) $K_2SO_4-D_1$ equals the inner section of $Li, K || SO_4, WO_4$. The melting curve consists of three branches with intersecting points at 23% K_2SO_4 and 546°, and 33.5% K_2SO_4 and 618°.

3) $K_2Cl_2-K_2SO_4$ is found to be the lateral side of the lower base of the prismatic composition, and represents a eutectic for the system with eutectic at 690° and 42% K_2SO_4 .

Results of the investigation on the inner sections are given in Fig. 4c. For such section, on the lateral sides of $D_1-K_2SO_4$, there appears a small area of K_2WO_4 separation, which wedges out rapidly within the system, and a triple eutectic point results at 490°.

Thus, the given section can be considered provisionally as stable, with a eutectic point at 490°, and composition: 12% K_2Cl_2 , 20% K_2SO_4 , 68% $Li_2WO_4 \cdot K_2WO_4$. The section dissects the volumes of crystallization: K_2Cl_2 , $Li_2WO_4 \cdot K_2WO_4$ complex, K_2SO_4 (α - and β -volumes) within the prism, and the wedging out area of the K_2WO_4 exchange product.

TABLE 3

Tetra- hedron	Character of the point	Composition (mole %)					Equilibrium phases
		Li'	K'	Cl'	SO ₄ '	WO ₄ '	
I }	Quaternary eutectic	64	36	78	18	4	$Li_2WO_4, Li_2Cl_2, K_2Cl_2, Li_2SO_4$
II }		80	20	20	64	16	$Li_2WO_4, D_1, Li_2SO_4, K_2Cl_2$
III	Quaternary transitional	73	27	18	43	39	$Li_2WO_4, D_1, D_2, K_2Cl_2$
IV }	Quaternary eutectic	42	58	10	32	58	$D_1, D_2, K_2SO_4, K_2Cl_2$
V }		27	73	16	12	72	$D_1, K_2Cl_2, K_2WO_4, K_2SO_4$

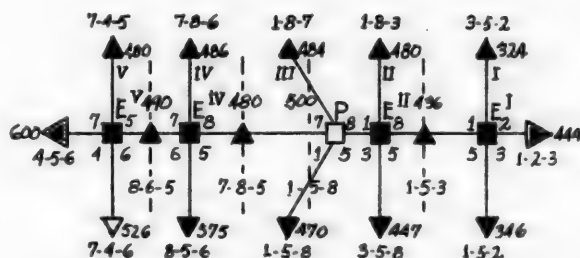


Fig. 7. Schemes of crystallization branching.

- 1) Li_2WO_4 ; 2) Li_2Cl_2 ; 3) Li_2SO_4 ; 4) K_2WO_4 ;
5) K_2Cl_2 ; 6) K_2SO_4 ; 7) D_1 ; 8) D_2 . E - Eutectic point (quaternary); P quaternary transition point; I, II, III, IV, V - tetrahedrons.

Unstable section $K_2Cl_2-D_1$ (76.5% $Li_2SO_4 + 23.5\% K_2SO_4$)* (Fig. 4d). The given section was investigated for the purpose of clarifying expansion inside the prismatic composition of the $Li, K || Cl, SO_4$ system, for the compound $2Li_2SO_4 \cdot K_2SO_4$ (2:1), melting with decomposition, the so-called lithium "langbeinite". In Fig. 4d is given a projection diagram of the investigated section for triangular composition. The given section dissects 3 volume crystallizations within the prism: K_2Cl_2 and two complexes, $Li_2SO_4 \cdot K_2SO_4$, and $Li_2WO_4 \cdot K_2WO_4$. The crystallization areas converge at the monovariant point, 492°, for the composition 21% Li_2WO_4 , 24% K_2Cl_2 , 55% $Li_2WO_4 \cdot K_2WO_4$. Thorough investigation of this profile did not show formation of widespread lithium langbeinite, $2Li_2SO_4 \cdot K_2SO_4$ within the prismatic composition of the $Li, K || Cl, SO_4, WO_4$ reciprocal system. The indicated section was found to be unstable, non-triangulating, and non-participating in the scheme of crystallization branching for the prism composition.

Combination of three book sections and of four diagonal ternary sections makes it possible to obtain a clear idea about the structure of the prism, as well as the chemism between components, and about the indicated reaction shifts in the melts.

* Provisionary symbol, L equals (76.5% $Li_2SO_4 + 23.5\% K_2SO_4$).

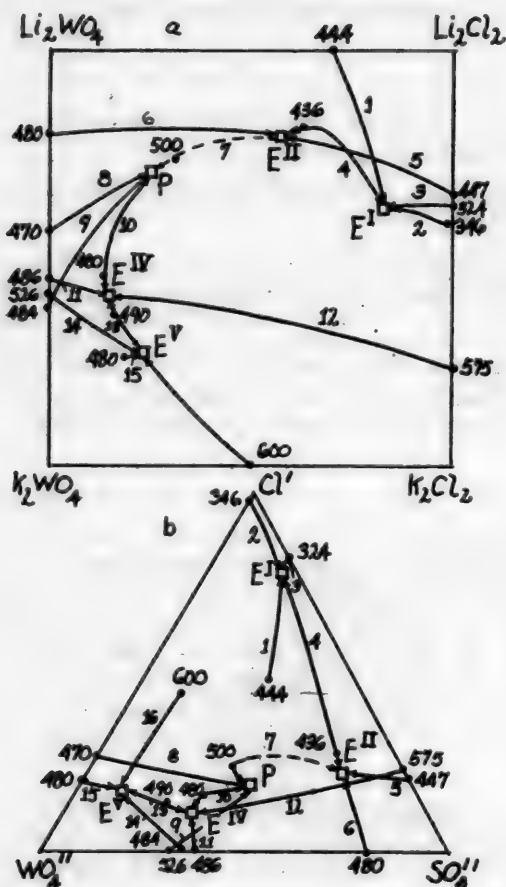


Fig. 8. Projection of crystallization branching on the lateral facet square of Li, K || Cl, WO₄ and the base triangle, K || Cl, SO₄, WO₄. Explanation in text and in Table 4.

TABLE 4

Data on Orthogonal Projection of Li, K || Cl, SO₄, WO₄ System and on the Li, K || Cl, WO₄ Square*

No.	Temperature	System	% Li'	% K'	% Cl'	% WO ₄ '	Solid phases
1	444°	Li ₂ WO ₄ -Li ₂ Cl ₂ -Li ₂ SO ₄	100	—	70	30	Li ₂ WO ₄ , Li ₂ Cl ₂ , Li ₂ SO ₄
2	346	Li ₂ WO ₄ -K ₂ Cl ₂ -Li ₂ Cl ₂	59	41	98	2	Li ₂ WO ₄ , K ₂ Cl ₂ , Li ₂ Cl ₂
3	324	Li ₂ SO ₄ -K ₂ Cl ₂ -Li ₂ Cl ₂	65	35	100	—	Li ₂ SO ₄ , K ₂ Cl ₂ , Li ₂ Cl ₂
4	436	Li ₂ WO ₄ -K ₂ Cl ₂ -Li ₂ SO ₄	82.5	17.5	62.5	37.5	Li ₂ WO ₄ , K ₂ Cl ₂ , Li ₂ SO ₄
5	447	Li ₂ SO ₄ -K ₂ Cl ₂ -D ₂	65	35	100	—	Li ₂ SO ₄ , K ₂ Cl ₂ , D ₂
6	480	Li ₂ WO ₄ -D ₁ -Li ₂ SO ₄	80	20	—	100	Li ₂ WO ₄ , D ₁ , Li ₂ SO ₄
7	500	Li ₂ WO ₄ -K ₂ Cl ₂ -D ₂	74	26	31	69	Li ₂ WO ₄ , K ₂ Cl ₂ , D ₂
8	470	Li ₂ WO ₄ -K ₂ Cl ₂ -D ₁	56.5	43.5	25	75	Li ₂ WO ₄ , K ₂ Cl ₂ , D ₁
9	484	Li ₂ WO ₄ -D ₁ -D ₁	38	62	—	100	Li ₂ WO ₄ , D ₁ , D ₁
10	480	D ₁ -D ₂ -K ₂ Cl ₂	43	57	14	86	D ₁ , D ₂ , K ₂ Cl ₂
11	575	D ₁ -K ₂ Cl ₂ -K ₂ SO ₄	24	76	100	—	D ₁ , D ₂ SO ₄ , K ₂ Cl ₂
12	486	D ₁ -D ₂ -K ₂ SO ₄	45	55	—	100	D ₁ , D ₂ , K ₂ SO ₄
13	490	D ₁ -K ₂ SO ₄ -K ₂ Cl ₂	36	64	16.5	83.5	D ₁ , K ₂ Cl ₂ , K ₂ SO ₄
14	526	D ₁ -K ₂ WO ₄ -K ₂ SO ₄	41	59	—	100	D ₁ , K ₂ WO ₄ , K ₂ SO ₄
15	480	D ₁ -K ₂ WO ₄ -K ₂ Cl ₂	26	74	19	81	D ₁ , K ₂ WO ₄ , K ₂ Cl ₂
16	600	K ₂ WO ₄ -K ₂ SO ₄ -K ₂ Cl ₂	—	100	50	50	K ₂ WO ₄ , K ₂ SO ₄ , K ₂ Cl ₂

* Composition after recalculating for Cl' and WO₄' ions is given in the Table.

The prismatic system Li, K || Cl, SO₄, WO₄ composition diagram is divided into 8 principal crystallization volumes of salts (Fig. 5): two complexes D₂-Li₂SO₄·K₂SO₄ and D₁-Li₂WO₄·K₂WO₄ and six components Li₂Cl₂, Li₂SO₄, Li₂WO₄, K₂Cl₂, K₂SO₄, and K₂WO₄, where the lithium chloride, sulfate and tungstates are divided into sections with α- and β-modifications. The largest crystallization volume occurs with potassium chloride. The complex compound, Li₂SO₄·K₂SO₄, penetrates deeply into the system and occupies quite completely a large volume relative to the total pyramidal volume.

The volume of the Li₂WO₄·K₂WO₄ complex is much smaller and constitutes approximately 1/2 of the sulfate complex volume.

The prism studied by four sections Li₂WO₄-K₂Cl₂-Li₂SO₄; Li₂WO₄-Li₂SO₄·K₂SO₄-K₂Cl₂; Li₂WO₄-K₂WO₄-Li₂SO₄·K₂SO₄-K₂Cl₂; and Li₂WO₄·K₂WO₄-K₂SO₄-K₂Cl₂ is divided into 5 tetrahedrons representing provisional independent quaternary systems (Fig. 6).

I) tetrahedron Li₂WO₄-K₂Cl₂-Li₂SO₄-Li₂Cl₂;

II) Li₂WO₄-D₂-K₂Cl₂-Li₂SO₄;

III) D₁-D₂-K₂Cl₂-Li₂WO₄;

IV) D₁-D₂-K₂Cl₂-K₂SO₄;

V) D₁-K₂Cl₂-K₂SO₄-K₂WO₄.

Of the four triangulating sections, three are found to be provisionally stable, and the quaternary Li₂WO₄·K₂WO₄-Li₂SO₄·K₂SO₄-K₂Cl₂ is clearly stable; the reciprocal prism system can, therefore,

be converted by these four sections into five tetrahedrons, of which not one, in the true sense, is a quaternary system, but rather is a quasi-quaternary system, since the volumes of the lateral complexes penetrate partially into the "foreign" tetrahedrons.

Each tetrahedron possesses one quaternary eutectic point and tetrahedron II — a transitional quaternary point. Their compositions are given in Table 3.

Schemes for the crystallization branching of the investigated quaternary reciprocal system are given in Fig. 7. On it are depicted triangulation planes (3, 4, 5, 6) and tetrahedrons formed by them (I, II, III, IV, V) as well as the triple eutectic and transitional points merging into the corresponding quaternary points. Projection of crystallization branching for the prism base $K \parallel Cl, SO_4, WO_4$ (Fig. 8a) and the side facet $Li, K \parallel Cl, WO_4$ (Fig. 8b) give a clear concept concerning distribution of the crystallization volumes of the salts, and the quaternary eutectic and transitional points. To construct the crystallization projection, the ionic composition for the triple eutectic points of the system was calculated, intersection points for the profiles through the prism with monovariant equilibrium curves given in Table 4.

Position of the quaternary points of the crystallization branching projections is provisionally found approximately. It can be made precise by plotting additional intersections on the prism; however, for solving the designated problem of disclosure of the general scheme for structure of the prism, the intersections completed in the prism were found sufficient.

As a general conclusion about the prism for the complex quaternary reciprocal system $Li, K \parallel Cl, SO_4, WO_4$, it can be pointed out that 1) investigation and determination of the eight basic crystallization volumes for six components and two complexes has been demonstrated, and that both complexes, $Li_2SO_4 \cdot K_2SO_4$ and $Li_2WO_4 \cdot K_2WO_4$ inside the quaternary system are stable; 2) for the $Li, K \parallel SO_4, WO_4$ system, there is a marginal non-diagonal system, the general character of which, on the whole, determines the character of the quaternary system, which is indicated by the simple eutectic character of the most interesting section $Li_2WO_4 \cdot K_2WO_4 - Li_2SO_4 \cdot K_2SO_4 - K_2Cl_2$.

SUMMARY

1. Five internal triangular sections through the composition prism have been studied, and it was established that $K_2Cl_2 - Li_2WO_4 - Li_2SO_4$ is a conditionally stable section with triple eutectic points at 436° ; $K_2Cl_2 - D_1 - D_2$, definitely stable section with eutectic point at 480° ; $K_2Cl_2 - Li_2WO_4 - D_2$ conditionally stable with transition point at about 500° ; $K_2Cl_2 - K_2SO_4 - D_1$ provisional stability, with eutectic point at 490° ; $K_2Cl_2 - D_1 - Li$ unstable, non-tetrahedron forming, non-participating in the formation of crystallization branching.

2. It has been established that the system is divided into 5 tetrahedrons by the four intersecting planes. In Table 3 the composition of the eutectic points for the tetrahedrons has been given.

3. The branching crystallization for the quaternary reciprocal system of $Li, K \parallel Cl, SO_4, WO_4$ has been constructed.

4. Projections of the crystallization branching have been constructed for the prism base, $K \parallel Cl, SO_4, WO_4$, and for the lateral facet, $Li, K \parallel Cl, WO_4$.

5. The character and evolutionary scheme for the prism facets studied have been determined for the system $Li, K \parallel Cl, SO_4, WO_4$.

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* T.p. = Consultants Bureau Translation pagination.

1. The first part of the paper discusses the importance of the study of the history of the United States. It is argued that a knowledge of the past is essential for a full understanding of the present and for the development of a sound policy for the future. The author points out that the study of history is not only a means of satisfying a natural curiosity about the past, but also a means of developing a sense of responsibility for the future.

2. The second part of the paper discusses the importance of the study of the history of the United States. It is argued that a knowledge of the past is essential for a full understanding of the present and for the development of a sound policy for the future. The author points out that the study of history is not only a means of satisfying a natural curiosity about the past, but also a means of developing a sense of responsibility for the future.

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SOLUBILITY OF AMMONIUM METAVANADATE IN AQUEOUS AMMONIUM CHLORIDE SOLUTIONS

V. V. Andreev

The salting-out effect of ammonium chloride on ammonium metavanadate aqueous solutions is widely applied in practice of isolation and quantitative determination of vanadium, as well as during the preparation of ammonium metavanadate and its purification by recrystallization from ammonium chloride aqueous solution, or by washing with similar solutions. These processes are frequently mentioned in literature dealing with the subject; however, the data given are contradictory. Thus, according to some directions, separation of ammonium metavanadate should be carried out in boiling or hot solutions [1-5], and according to others, at 30-40° [6], while yet another recommendation is to salt it out in the cold [7, 8]. The ammonium chloride, according to a number of procedures, is introduced into the ammonium metavanadate solution in solid form, and according to others, in the form of saturated or concentrated aqueous solutions. Some recommend introduction of ammonium chloride into ammonium metavanadate solution up to the point of saturation [6, 8, 9], and use of an excess of the salting-out agent [7, 10, 11, 12], while others even consider 10-12% [13, 14], or even 0.9-1.3% ammonium chloride [13, 15] to be adequate. One opinion maintained is that ammonium chloride salts out ammonium metavanadate completely, while yet other works deny this [6, 12, 16]. A number of authors recommend washing the ammonium vanadate with concentrated or saturated aqueous ammonium chloride solution [5-7, 9, 12, 17-21], while others recommend for this purpose 2% [3, 15] and 1% [22] solutions.

In order to clarify this problem, an investigation of the solubility of ammonium metavanadate in aqueous ammonium chloride solutions was undertaken; for this purpose, the generally accepted method was used, consisting of a determination of solution concentrations while maintaining equilibrium by continuous stirring of the chemically-pure salts with distilled water in a water thermostat equipped with electrical heater and thermoregulator. The ammonium metavanadate in all experiments was introduced in such excess as to ensure its presence in the bottom phase, the quantity of ammonium chloride being varied at will. Investigation was carried out at 35° and at 60°. The solubility, in addition, was determined at room temperature ($12.5 \pm 2.0^\circ$). During analysis of the solutions and of the lower residues, the V content was determined colorimetrically with hydrogen peroxide in acid medium [18, 23], and Cl by titration with silver nitrate solution in the presence of nitric acid. Attainment of equilibrium was determined by coincidence in analytical data for two samples taken successively over a specified time interval. The quantities of V and Cl found were recalculated for NH_4VO_3 and NH_4Cl contents. Concentration calculation was carried out for 100 g of water and 100 g of solution. Resulting data are given in the table. Values for ammonium chloride solubility in water were taken from the literature data. Composition of the solid phase was determined by means of triangle solubility diagrams.

It can be seen from the table first of all that ammonium metavanadate solubility values, calculated for 100 g of water and for 100 g of solution, are almost identical. By means of triangle solubility diagrams, it was determined that at the indicated temperatures, neither crystalline hydrates nor double salts are formed in the system investigated.

Values obtained for solubility of ammonium metavanadate in water agree with the data of Zolotavin [26] and Meyer [2], and differ sharply (by 10-fold) from the values given in the reference manual of Lurye [27], which were found to be, as is not too difficult to determine, interpolated and 10-fold greater than the data of Meyer, differing as well from the data of Lachartre [28], regarding which an assumption has been voiced that they are 10-fold greater [29]. Pascal [30] gives corrected data on Lachartre. There is no doubt that Lurye and Lachartre have introduced an error, having incorrectly presented signs for solubility values, or having written 100 for the quantity of water in the directions instead of 1000. It is to be regretted that erroneously written data are being transcribed from one reference manual to another at present as well as previously.

The polythermic diagram constructed according to the table data is given in Fig. 1.

TABLE
Solubility of Ammonium Metavanadate in Aqueous Ammonium Chloride Solutions

No.	Temperature	Content in solution in g/ 100 g				Composition of moist bottom residue, wt. percent		Solid phase
		Water		Solution		NH ₄ VO ₃	NH ₄ Cl	
		NH ₄ VO ₃	NH ₄ Cl	NH ₄ VO ₃	NH ₄ Cl			
1	12.5° ± 2.0°	0.440	—	0.440	—	—	—	NH ₄ VO ₃
2	12.5° ± 2.0	0.085	0.262	0.085	0.261	—	—	—
3	12.5 ± 2.0	0.018	0.553	0.018	0.550	77.07	not found	NH ₄ VO ₃
4	12.5 ± 2.0	not found	2.320	not found	2.270	—	—	—
5	13°	—	33.900	—	25.300	—	—	NH ₄ Cl
6	35°	1.150	—	1.140	—	—	—	NH ₄ VO ₃
7	35	0.500	0.298	0.497	0.296	83.19	not found	NH ₄ VO ₃
8	35	0.172	0.727	0.171	0.721	—	—	—
9	35	0.150	1.080	0.149	1.067	—	—	—
10	35	0.081	1.600	0.080	1.574	44.62	2.00	NH ₄ VO ₃
11	35	0.027	2.610	0.026	2.540	30.44	1.84	NH ₄ VO ₃
12	35	0.006	4.680	0.006	4.470	—	—	—
13	35	traces	9.870	traces	8.980	—	—	—
14	35	not found	12.920	not found	11.440	21.44	9.22	NH ₄ VO ₃
15	35	not found	42.490	not found	29.820	20.13	76.65	NH ₄ VO ₃ and NH ₄ Cl
16	35°	—	43.600	—	30.400	—	—	NH ₄ Cl
17	60°	2.550	—	2.490	—	—	—	NH ₄ VO ₃
18	60	0.562	1.370	0.551	1.340	—	—	—
19	60	0.220	2.560	0.210	2.490	57.77	0.49	NH ₄ VO ₃
20	60	traces	25.090	traces	20.060	—	—	—
21	60	not found	53.520	not found	34.860	—	—	—
22	60°	—	55.200	—	35.600	—	—	NH ₄ Cl

• [24].
•• [25].
••• [13].

Because of strong salting out of ammonium metavanadate with ammonium chloride, there is no crystallization area of the latter on the diagram.

The almost quantitative salting-out of ammonium metavanadate is readily attainable at various temperatures, and does occur, as the solubility data indicate, at the following concentrations in solution of ammonium chloride: at 12.5° about 1.5, at 35° about 10.0, and at 60° about 25.0 g per 100 g of water. These values presented in Fig. 2 show the limit for complete salting-out of ammonium metavanadate. In the same figure is given a section of the solubility curve for ammonium chloride in water.

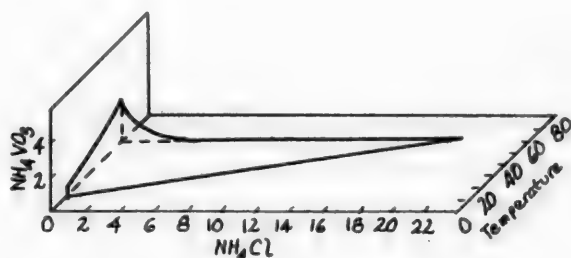


Fig. 1. Polythermal diagram of solubility (in g/100 g of the solution) in the $\text{NH}_4\text{VO}_3\text{-NH}_4\text{Cl-H}_2\text{O}$ system from 12.5 to 60°.

It can be seen in Fig. 2 that complete salting-out of ammonium metavanadate occurs in solution not saturated with ammonium chloride. This attests to the impracticability of introducing excessive amounts of ammonium chloride, or of bringing the solutions up to saturation with ammonium chloride, as recommended by a number of authors, as well as the use of saturated versus concentrated solutions of ammonium chloride for washing the ammonium metavanadate.

As can be seen from the data given, with increased temperature ammonium chloride consumption increases during salting out. Thus, upon introducing solid ammonium chloride into ammonium metavanadate solution, there is required per 1 part by weight of the latter, for its complete isolation: at 12.5° $1.5:0.44 = 3.4$, at 35° $10.0:1.15 = 8.7$ and at 60° $25.0:2.55 = 9.4$ parts by weight of NH_4Cl . Consumption of ammonium chloride is considerably decreased as the ammonium metavanadate precipitation is carried out from saturated solutions at increased temperatures, and the amount of ammonium chloride by calculating for complete salting out of ammonium metavanadate in the cold.

The minimal quantity of ammonium chloride required in this case should be calculated according to the equation $x = \frac{a \cdot b}{100}$, where a is the quantity of ammonium chloride in weight percent of the quantity of water, determined by means of a salting-out curve for a specified cooling temperature of the solution; b is the quantity of water in the solution; and x is the quantity of ammonium chloride sought for. Thus, for example, given the case of an aqueous saturated solution of ammonium metavanadate at 60° which is then cooled to 12.5°, the ratio between minimum required amount of ammonium chloride and the quantity of ammonium metavanadate, will be equal to $1.5:2.55 = 0.6$. Upon saturating ammonium metavanadate solution at higher temperature, and with a subsequent more extensive cooling (cooling to a lower temperature than before), the value for the ratio investigated is lowered even more.

Some authors recommend applying an aqueous solution of ammonium chloride instead of the solid, during the isolation of ammonium metavanadate. This is quite feasible under the conditions for ensuring proper concentration of ammonium chloride which is in direct relation to the value, b , in the equation quoted above.

An ammonium chloride concentration equal to 10-20% as recommended by some authors, is inexpedient, since it is only justifiable in those cases where salting out is carried out at 40°. A concentration of ammonium chloride equal to 1-2%, as recommended by other authors, is rational only when cooling below 12.5° is carried out.

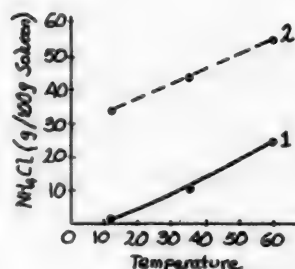


Fig. 2. Complete salting-out curves for ammonium metavanadate with ammonium chloride and solubilities of the latter in water. 1) Complete salting-out of NH_4VO_3 from aqueous solution; 2) NH_4Cl solubility in water.

SUMMARY

From data on combined solubility of ammonium metavanadate and ammonium chloride in water, the optimal conditions for separation and washing of ammonium metavanadate by the use of ammonium chloride can be determined.

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COMPOSITION OF THE SOLUBLE COMPLEX BETWEEN NICKEL COMPOUNDS AND DIMETHYLGLYOXIME FORMED IN THE PRESENCE OF OXIDANTS

L. S. Nadezhina and P. N. Kovalenko

A conscientious approach to the selection of a reaction suitable for colorimetric determination of any element is possible only under conditions of a detailed study of the basic physico-chemical characteristics for the colored compound in solution: its molar extinction coefficient, equilibrium constant, spectrophotometric characteristics, and so forth. An obscure conception of the chemism of the process does not permit theoretical substantiation of the suitability of any one reaction for quantitative determinations, and thus forces the investigator into the path of empirical selection of optimal conditions for each specific case. Compositions of a whole series of chemical compounds used in colorimetry have not been accurately characterized up to the present time.

Interaction of nickel salts with dimethylglyoxime, occurring in the presence of an oxidant, to form an intense orange-red colored compound is the basis of most colorimetric methods for determination of nickel. The chemism of the reaction, and the composition of the resulting compound, however, cannot be considered to have been accurately characterized. Numerous investigations of this reaction, carried out by various authors, have been directed chiefly to a study of the determination of nickel in various media and with various oxidants.

The composition of the nickel complex with dimethylglyoxime has been investigated by Feigl [1], who offered the hypothesis that the presence of an oxidant, Ni^{2+} ion converts into Ni^{4+} , the latter forming with dimethylglyoxime (H_2Dm) a brightly-colored compound corresponding to the formula $[\text{Ni}(\text{HDM})_2\text{O}]$.

This statement remained unchallenged for a long time, and only recently have there appeared papers in the literature again devoted to this problem. Thus, in the work of Hurman [2], there is found indication that nickel in the presence of an oxidant forms two types of colored compounds — with two and four molecules of dimethylglyoxime, which do not separate from each other. In subsequent works, Hurman's opinion did not find support, and so was not developed further. Babko has carried out extensive and systematic investigation of the chemistry of this reaction, using I_2 as the oxidant, and has proposed a theory that in course of reaction, the dimethylglyoxime, and not nickel, is oxidized, and that the colored compound formed during the reaction is found to be a complex ion of divalent nickel with unstable oxidation products of dimethylglyoxime [3]. In such case, formation of several kinds of complexes can be assumed. Experiments by Andreev and Azrelyan [4] did not confirm this assumption of Babko, but on the contrary, led the authors to a conclusion that nickel is oxidized in the reaction course. In contrast to Feigl, Andreev and Azrelyan consider that nickel goes to the trivalent, and not the tetravalent, state, entering as such into the composition of the complex. The work of Yatsimirsky [5] gives reason to believe that there may possibly exist two types of soluble nickel complexes with dimethylglyoxime (one with three, and one with a single molecule of H_2Dm , the latter complex being colorless).

From what has been indicated above, there are indications that the chemistry of formation of soluble nickel complexes with dimethylglyoxime cannot be considered yet as having been completely worked out; the authors, therefore, have studied the fundamental physico-chemical characteristics of this complex in the presence of various oxidants in order to define more closely data which are already available on the composition of the complex.

EXPERIMENTAL

Work was carried out on a photoelectric colorimeter, FEK-2, equipped with galvanometer, with a sensitivity of $5 \cdot 10^{-7}$ A/mm/m. Optical density of the solution (D) was determined by the differential method, using light filters whose characteristics were λ 500 m μ , λ 550 m μ , and λ 450 m μ . I_2 , Br_2 , $\text{K}_3[\text{Fe}(\text{Cn})_6]$ and $(\text{NH}_4)_2\text{S}_2\text{O}_8$ were used as oxidants. Investigation of the effects of NH_4OH and of NaOH upon the D value indicated beforehand that the latter is not dependent upon their concentrations in the solution. In all subsequent experiments, therefore, the NaOH or NH_4OH concentration was kept equal to 0.5 M.

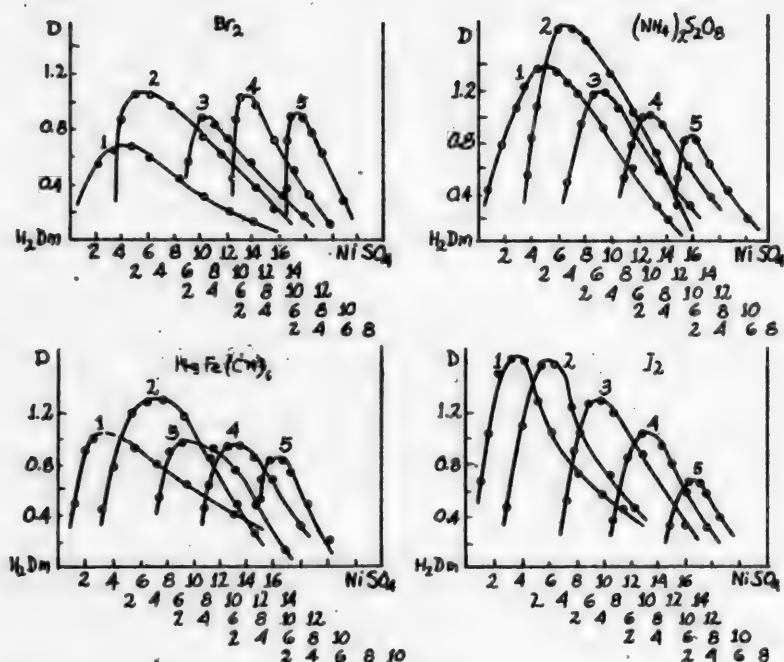


Fig. 1. NiSO_4 - H_2Dm -Ox system in ammoniacal medium. Composition is given in milliliters of 0.01 M solutions. Total volume of a mixture of the three components is 20 ml. Quantity of oxidant: 1) 4 ml; 2) 6 ml; 3) 8 ml; 4) 10 ml; 5) 12 ml.

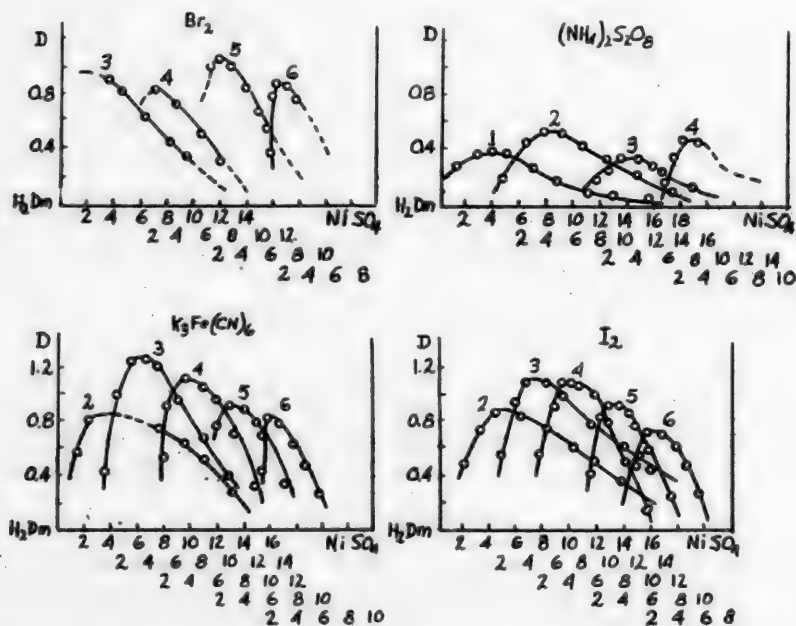


Fig. 2. NiSO_4 - H_2Dm -Ox system in alkaline medium. Composition is given in milliliters of 0.01 M solutions. The total volume of three-component mixture was 20 ml. The quantity of oxidant: 1) 2 ml; 2) 4 ml; 3) 6 ml; 4) 8 ml; 5) 10 ml; 6) 12 ml.

Physico-chemical analysis of the composition of nickel complexes with dimethylglyoxime in the presence of various oxidants. Using the physico-chemical analytical method developed by Babko [6] for the case of ternary systems, the authors investigated the following systems in alkaline and in ammoniacal media: $\text{NiSO}_4\text{--H}_2\text{Dm--I}_2$, $\text{NiSO}_4\text{--H}_2\text{Dm--Br}_2$, $\text{NiSO}_4\text{--H}_2\text{Dm--K}_3[\text{Fe}(\text{CN})_6]$, $\text{NiSO}_4\text{--H}_2\text{Dm--}(\text{NH}_4)_2\text{S}_2\text{O}_8$, as well as the system $\text{NiSO}_4\text{--H}_2\text{Dm}$ in alkaline medium (in the latter case, oxygen of the air playing the role of oxidant). In a general way, composition of the investigated system can be expressed in the form of a tetrahedron whose peak is the solvent, water, and whose base is the triangle $\text{NiSO}_4\text{--H}_2\text{Dm--Ox}$ (where Ox. is the oxidant).

For a more complete characterization of the system, the authors studied four sections of the tetrahedron, parallel to the base, with concentrations for initially equimolar solutions, equal, respectively, to 0.006, 0.008, 0.010, 0.012 M. Investigation was carried out parallel to the $\text{NiSO}_4\text{--H}_2\text{Dm}$ side.

Optical density of the solution was measured at various sections of the spectrum, but in all cases the D maximum corresponded to the same composition; therefore, in Figs. 1-2, only data obtained from work with the green light filter (λ 500 m μ) are presented.

In some cases formation of nickel hydroxide of $\text{Ni}(\text{HDm})_2$ was observed. These sections of the curves remain uninvestigated, and are shown by the dotted line in such cases where they could be extrapolated. In both alkaline and ammoniacal media, the extinction maximum of the solutions corresponded in almost all cases to a ratio of $\text{NiSO}_4\text{:H}_2\text{Dm} = 1:3$ (Figs. 1 and 2).

The colored compound from nickel and dimethylglyoxime obtained in the absence of oxidant (Fig. 3) is in no way distinctive in its spectrophotometric characteristics from the analogous complexes obtained in the presence of I_2 , Br_2 , $\text{K}_3[\text{Fe}(\text{CN})_6]$ and $(\text{NH}_4)_2\text{S}_2\text{O}_8$. However, the time required for establishment of maximum intensity in color for the first case is much longer and depends to a considerable extent upon the NaOH concentration of the solution. Thus, for example, maximum coloration in 0.1 N NaOH is observed after 2.5 hours, and in 1.0 N NaOH after only 30 minutes.

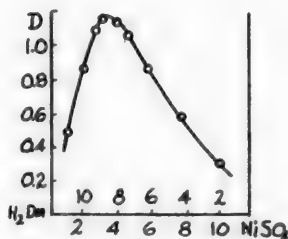


Fig. 3. $\text{NiSO}_4\text{--H}_2\text{Dm}$ system in 0.5 N NaOH. Oxidant: oxygen of the air. Composition given in milliliters of 0.01 M solutions. Total volume of two-component mixture was 12 ml.

For general characterization of the $\text{NiSO}_4\text{--H}_2\text{Dm--Ox}$ ternary system, the triangles were constructed, on which curves were plotted, connecting points with same color intensity (isochromes) and making it possible to estimate the composition of the soluble complex of nickel with dimethylglyoxime (Figs. 4 and 5). For visual convenience, straight lines were plotted in the triangles, corresponding to the sections $\text{NiSO}_4\text{·3H}_2\text{Dm--Ox}$, $\text{NiSO}_4\text{·2H}_2\text{Dm--Ox}$, $\text{NiSO}_4\text{·2Ox--H}_2\text{Dm}$.

In all cases, the center of the isochromes was situated on a straight line, $\text{NiSO}_4\text{·3H}_2\text{Dm--Ox}$. This made it possible to assume that Ni reacts with dimethylglyoxime in a ratio of 1:3, independently of the nature of the oxidant. The ratio of $\text{NiSO}_4\text{:Ox}$, however, apparently depends upon the nature of the oxidant, and is not found to be a whole number, but fluctuates within the range of 1.5-2.5.

Because of this fact, the experimentally-obtained isochromic centers, in most cases, were not located on the $\text{NiSO}_4\text{--2Ox--H}_2\text{Dm}$ straight line.

Investigation of the complex composition according to the method of logarithmic limits. Apart from the physico-chemical analytical method, data on the ratio between reacting components can be obtained by using the method of logarithmic limits. The latter is based upon utilization of a directly proportional function between the logarithm of the concentration of complex-forming materials and the logarithm of the solution's optical density. Upon plotting these values on a coordinate axis, a straight line results, the tangent of which corresponds to the number of H_2Dm groups bound with nickel.

The authors' investigations were carried out with nickel sulfate solution of concentration equal to $2.07 \cdot 10^{-4}$ M. Dimethylglyoxime was varied in the concentration range $0.08 \cdot 10^{-3}$ – $10 \cdot 10^{-3}$ M. Concentration of oxidant was maintained constant in all cases and was equal to $2.0 \cdot 10^{-3}$ M. Measurements were carried out with different light filters, and in all cases analogous data were obtained.

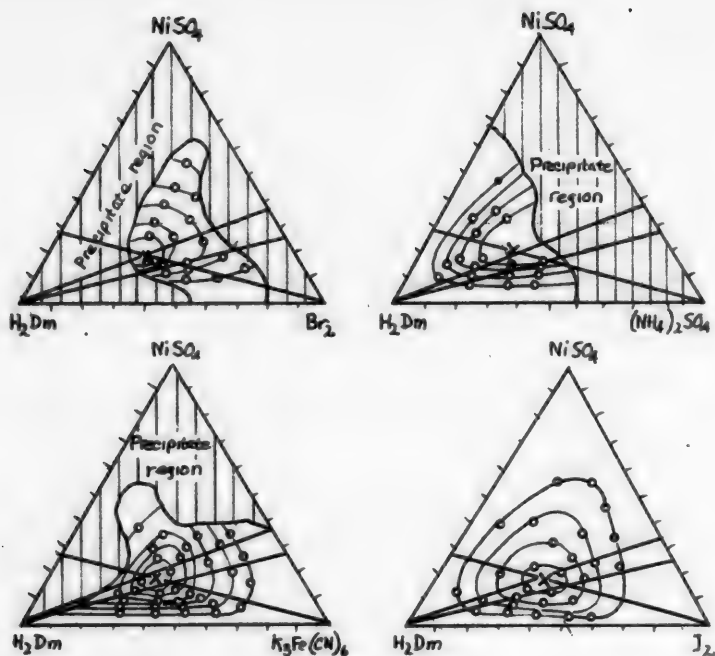


Fig. 4. Isochrome triangles for NiSO_4 - H_2Dm -Ox system in alkaline medium. Concentration of initial solutions of NiSO_4 , H_2Dm and Ox. was 0.1 M. Total volume of three-component mixture was 30 ml.

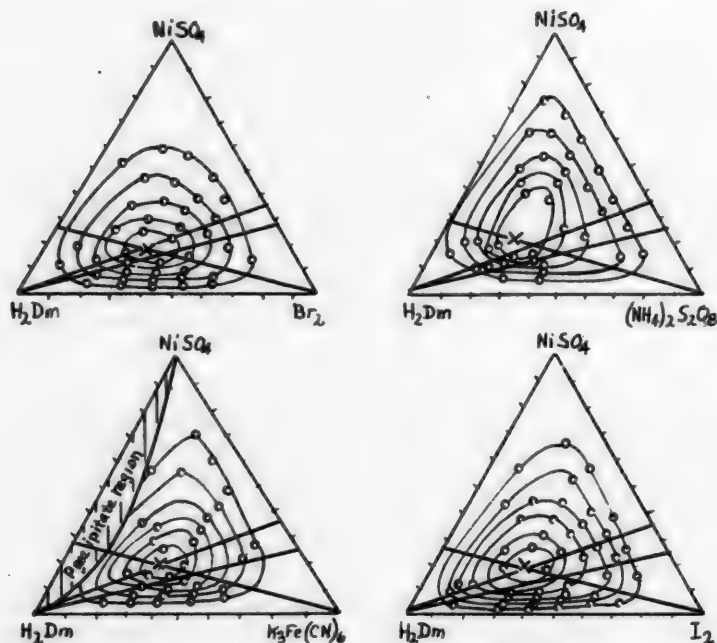


Fig. 5. Isochrome triangles for the system NiSO_4 - H_2Dm -Ox in ammoniacal medium. Concentration of initial solutions of NiSO_4 , H_2Dm and Ox. was 0.01 M. Total volume of three-component mixture was 20 ml.

In the table and in Fig. 6 results obtained from work with the green filter (λ 550 m μ) are given.

Data on the relationship between optical density of the solution to concentration of dimethylglyoxime obtained during work with different oxidants indicate that the type of oxidant does not affect the character of the reaction between nickel and dimethylglyoxime to any great extent. It became evident during a plot of the logarithmic graph (Fig. 6) that in both alkaline and ammoniacal media the n value, which characterizes the number of H_2Dm molecules entering into the complex composition, is close to three, which completely substantiates the data obtained by the method of physico-chemical analysis.

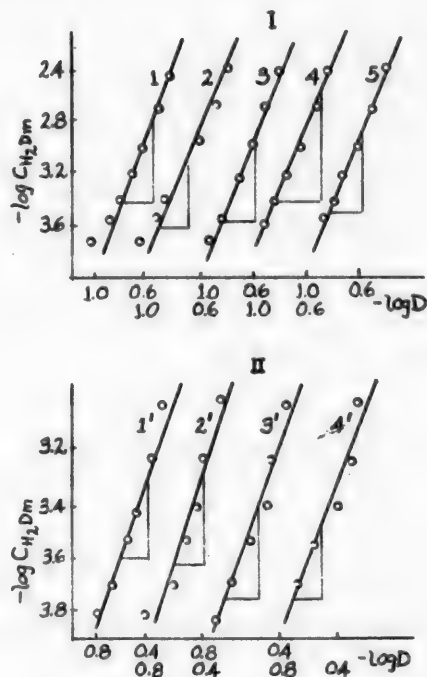


Fig. 6. Optical density as a function of the H_2Dm concentration in solution. I) Alkaline medium; II) ammoniacal medium. 1) I_2 ($tg \angle = 3.0$); 2) Br_2 ($tg \angle = 2.6$); 3) $(NH_4)_2S_2O_8$ ($tg \angle = 2.9$); 4) $K_3Fe(CN)_6$ ($tg \angle = 2.7$); 5) O_2 ($tg \angle = 2.9$); 1') I_2 ($tg \angle = 3.1$); 2') Br_2 ($tg \angle = 3.3$); 3') $K_3Fe(CN)_6$ ($tg \angle = 2.9$); 4') $(NH_4)_2S_2O_8$ ($tg \angle = 2.7$).

firmly by a number of other authors, it is quite reasonable to assume, as has already been expressed by Andreev and Azrelyan [4], that in the course of reaction, oxidation of Ni^{2+} to Ni^{3+} occurs, and that the latter then forms the soluble, bright-colored complex with three molecules of dimethylglyoxime.

The oxidation process $Ni^{2+} \rightleftharpoons Ni^{3+}$ has been found to be readily reversible, and depends upon the nature of the oxidant; the ratio of $NiSO_4$: Ox, therefore, does not remain constant. In the given case, the K_e for the reaction is sufficiently large to ensure an equilibrium shift to the side of the oxidized form, under conditions of negligible nickel concentration in the solution. With considerable $NiSO_4$ concentration (of the order of $1 \cdot 10^{-3} M$ and greater) the soluble complex fails to form, even in the presence of excess oxidant, and the usual precipitate, $Ni(HDm)_2$, results. On the other hand, in the presence of large amounts of oxidant (0.1-1.0 M) there is observed decoloration of the solution, which is connected with oxidation of the dimethylglyoxime, since the addition of new H_2Dm to the solution renews the color.

Trivalent nickel compounds are not very numerous, but they do exist and are of sufficient stability. Ni_2O_3 is widely used in qualitative analysis. Hofman describes the Ni^{3+} complex with formoxime prepared by him, corresponding to the formula $Na_3[Ni(CH_2NO)_3]$ [1]; other specifications are available, indicating the possibility of compound formation in which nickel has a valency equal to 3. Moreover, by analogy with cobalt, which in almost all complexes is trivalent, Ni^{3+} should also give complexes whose K_e 's are sufficiently great, thus ensuring shift of equilibrium to the side of formation of the oxidized form. The composition of the complex can then be represented by the formula $Ni(HDm)_3$.

The section cut by a straight line on the abscissa axis at the equilibrium H_2Dm concentration equal to 1.0 M is directly related to the value for the equilibrium constant (K_e). This constant was calculated by Yatsimirsky [5] during the investigation of the reaction between nickel and dimethylglyoxime in the absence of oxidant and with prolonged standing of the ammoniacal solution (the role of oxidant being fulfilled by oxygen of the air) and was found equal to 10^{14} . The authors' data ($K_e = 1.4 \cdot 10^{12}$) are in sufficiently good agreement with the results of Yatsimirsky's calculations, and indicate that in all cases where formation of a soluble colored nickel complex takes place the nature of the oxidant affects only the process rate, and not its chemism.

EVALUATION OF RESULTS

The results obtained lead one to think that despite Babko's opinion [3], the oxidant does react with nickel but not with dimethylglyoxime, since, in such a reaction, stoichiometric ratios between the volumes of equimolar solutions of H_2Dm and oxidant would have been expected. Inasmuch as the hypothesis concerning unstable oxidation products of dimethylglyoxime capable of reacting with Ni^{2+} ions is concerned, which was not con-

TABLE

No.	Concentra- H ₂ Dm·10 ³ M	D (ammoniacal medium)				D (alkaline medium)				
		I ₂	Br ₂	(NH ₄) ₂ S ₂ O ₈	K ₃ Fe(CN) ₆	I ₂	Br ₂	(NH ₄) ₂ S ₂ O ₈	K ₃ Fe(CN) ₆	O ₂
1	0.08	0.070	0.080	—	0.070	—	—	—	—	—
2	0.10	0.120	0.140	0.070	0.120	—	—	—	—	—
3	0.16	0.160	0.160	0.120	0.190	0.050	0.050	0.045	0.030	0.040
4	0.20	0.200	0.210	0.180	0.220	0.090	0.080	0.110	0.050	0.085
5	0.30	0.220	0.230	0.230	0.250	0.130	0.115	0.135	0.120	0.110
6	0.40	0.240	0.250	0.255	0.280	0.160	0.170	0.160	0.140	0.165
7	0.60	0.255	0.265	0.280	0.290	0.200	0.195	0.210	0.185	0.190
8	1.00	0.270	0.280	0.295	0.300	0.240	0.240	0.255	0.240	0.260
9	2.00	0.315	0.320	0.310	0.310	0.310	0.320	0.290	0.300	0.320
10	4.00	0.330	0.345	0.320	0.330	0.340	0.360	0.330	0.335	0.345
11	8.00	0.335	0.350	0.315	0.330	0.340	0.355	0.335	0.330	0.340
12	10.00	0.330	0.350	0.320	0.330	0.340	0.360	0.330	0.330	0.340

In a similar treatment, nickel plays the role of a complex former with a valency of three and a coordination number equal to six, which is characteristic for the majority of complex nickel compounds.

SUMMARY

1. Using a physico-chemical method of analysis, the characteristics of the following system have been studied: NiSO₄-H₂Dm-I₂, NiSO₄-H₂Dm-Br₂, NiSO₄-H₂Dm-K₃[Fe(CN)₆], NiSO₄-H₂Dm-(NH₄)₂S₂O₈, NiSO₄-H₂Dm-oxygen of the air.

2. It has been demonstrated that a complex is formed, corresponding to a ratio of NiSO₄:H₂Dm = 1:3, which is independent of the nature of the oxidant and the character of the medium.

3. Physico-chemical analytical data have been confirmed by calculation of the coordination number by the method of logarithmic limits.

4. A hypothesis has been advanced concerning the character of the interaction course with dimethylglyoxime in the presence of an oxidant.

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POLAROGRAPHIC REDUCTION OF ETHERS

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At the present time an increasing variety of organic substances are under polarographic investigation, among them ethers, the value of which is presently very prominent in the development of organic synthesis. There are a number of works dealing with polarographic determination of ethers [1-5]. Among these works, a number of saturated carboxylic acids have been polarographed, namely: the ethyl esters of mono- and of dicarboxylic acids (formic, acetic, butyric, isobutyric, valeric, caproic, capronic, caprylic, malonic, succinic, adipic and others) and certain esters of chloroacetic acids. Such esters with conjugated double bonds as dimethyl oxalate, dibutyl phthalate, methyl and butyl methacrylate, as well as the sulfonic acid esters, were polarographed.

It has been established that esters of the saturated mono- and dicarboxylic acids without the conjugated bond are not reduced at the dropping mercury electrode up to 2.2 V. Esters of chloroacetic acid and the above-mentioned esters with carbonyl bond, which are conjugated with the ethylenic bond, are reduced polarographically. Their half-wave potentials, diffusion current constants, and diffusion coefficients, have been determined.

In the present work, the authors have set up the task of determining the behavior of a series of simple vinyl ethers at the dropping mercury electrode, as well as some esters with the carbonyl bond, conjugated with the ethylenic bond, namely: methyl acrylate, methyl and butyl methacrylates and free methacrylic acid.

The polarographic behavior of simple vinyl ethers, as well as methyl acrylate and free methacrylic acid, have not been discussed in the literature. The half-wave potentials and diffusion current constants, and the diffusion coefficients for methyl methacrylate published in the literature differ among themselves noticeably.

EXPERIMENTAL

Objectives of the Work and Methods of Measurements

All vinyl ethers in Table 1, synthesized according to the Favorsky-Shostakovsky method [6], were supplied by M. F. Shostakovsky. The other ethers used were prepared by distillation of the technical products. The characteristics of the ethers investigated and methacrylic acid are given in Table 1.

Polarography was carried out with a Gorky polarograph M-7, with a mirror galvanometer of Banner Factory manufacture, with a sensitivity equal to 200 mm/ μ A at a scale distance of galvanometer from mirror of 100 cm. Shunts from $\frac{1}{5}$ to $\frac{1}{50}$ sensitivity were used in the work.

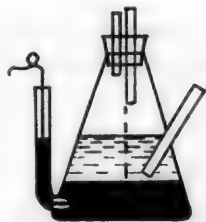


Fig. 1. Electrolyzer.

The vessel pictured in Fig. 1 was used for the electrolyzer. At the left is placed the current outlet from the anode, and at the right a tube for supplying nitrogen in order to remove oxygen from solution which is dissolved. Resistance of the electrolyzer for the solutions studied amounted to 3000 ohms.

Characteristics of the capillary during polarography of the vinyl ether was as follows: mass of the mercury drop, $m = 1.75$ mg; dropping period, $t = 3.25$ sec. Without a polarization voltage, the capillary constant was $m^{2/3} \cdot t^{1/6} = 1.507$ $\text{mg}^{2/3} \text{sec}^{-1/6}$.

The base electrolyte in the case of vinyl ethers was $(\text{CH}_3)_4\text{NI}$ ($c = 0.25$ mol/l in 75% $\text{C}_2\text{H}_5\text{OH}$) solution, as well as weak solutions of alkali and of acids. The vinyl ethers were polarographed in the concentration range from 1 to 15 mmol/l.

Esters with a carbonyl bond conjugated with an ethylenic bond were polarographed in the concentration range from 5 to 50 mmol/l; as the background electrolyte in this case, a more dilute solution $(\text{CH}_3)_4\text{NI}$ ($c = 0.1$ mol/l in 50% $\text{C}_2\text{H}_5\text{OH}$) was used.

TABLE 1

Name of compound and its formula	Boiling point	n_D^{20}
Vinylpropyl ether $\begin{array}{c} \text{CH}_3(\text{CH}_2)_2\text{O} \\ \diagup \\ \text{C}=\text{C} \\ \diagdown \quad \diagup \\ \text{H} \quad \text{H} \end{array}$	64-66°	1.3950
Vinylbutyl ether $\begin{array}{c} \text{CH}_3(\text{CH}_2)_3\text{O} \\ \diagup \\ \text{C}=\text{C} \\ \diagdown \quad \diagup \\ \text{H} \quad \text{H} \end{array}$	94	1.4026
Vinylisoamyl ether $\begin{array}{c} (\text{CH}_3)_2\text{CH}(\text{CH}_2)_2\text{O} \\ \diagup \\ \text{C}=\text{C} \\ \diagdown \quad \diagup \\ \text{H} \quad \text{H} \end{array}$	110-112	1.4065
Vinylnonyl ether $\begin{array}{c} \text{CH}_3(\text{CH}_2)_8\text{O} \\ \diagup \\ \text{C}=\text{C} \\ \diagdown \quad \diagup \\ \text{H} \quad \text{H} \end{array}$	205	1.4320
Vinylphenyl ether $\begin{array}{c} \text{C}_6\text{H}_5\text{O} \\ \diagup \\ \text{C}=\text{C} \\ \diagdown \quad \diagup \\ \text{H} \quad \text{H} \end{array}$	—	1.5220
Methyl acrylate $\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_2=\text{CH}-\text{C} \\ \diagdown \\ \text{OCH}_3 \end{array}$	80-83	1.403
Methyl methacrylate $\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_2=\text{C}-\text{C} \\ \quad \diagdown \\ \text{CH}_3 \quad \text{OCH}_3 \end{array}$	100	1.4158
Butyl methacrylate $\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_2=\text{C}-\text{C} \\ \quad \diagdown \\ \text{CH}_3 \quad \text{OC}_4\text{H}_9 \end{array}$	—	1.4228
Methacrylic acid $\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_2=\text{C}-\text{C} \\ \quad \diagdown \\ \text{CH}_3 \quad \text{OH} \end{array}$	161° (68.5° at 14 mm)	1.4310

For polarographing the esters, a capillary was used for which at 2.13 V the mass of the mercury drop, m , was equal to 0.64 mg. and the dropping period, t , was equal to 3.1 sec; the capillary constant in this case was, thus: $m^{2/3} \cdot t^{1/6} = 0.956 \text{ mg}^{2/3} \text{ sec}^{-1/6}$.

All values of half-wave potentials ($E_{1/2}$) found refer to the potential toward a saturated calomel electrode. The anode potential relative to the saturated calomel electrode was equal to 0.33 V, with some deviations in the case of individual esters.

Vinyl Ethers

Polarographed were: vinylpropyl, vinylbutyl, vinylisoamyl, vinylnonyl and vinylphenyl ethers.

Using $(\text{CH}_3)_4\text{NI}$ as the background electrolyte, as well as dilute solutions of alkalis and of acids, no diffusion waves were obtained for the enumerated vinyl ethers in Table 1.

Esters with Conjugated Double Bonds

Diffusion waves were obtained for methyl acrylate, free methacrylic acid, methyl and butyl methacrylates, using $(\text{CH}_3)_4\text{NI}$ as the background solution. During the transition from lower to higher concentrations, there appeared maxima in the range from 1.8 to 2.2 V on the polarograms.

The maxima were suppressed by gelatin solutions for the concentration range from 0.0075 to 0.0275 (relative to the overall volume of solution investigated). Comparing the polarograms without gelatin with polaro-

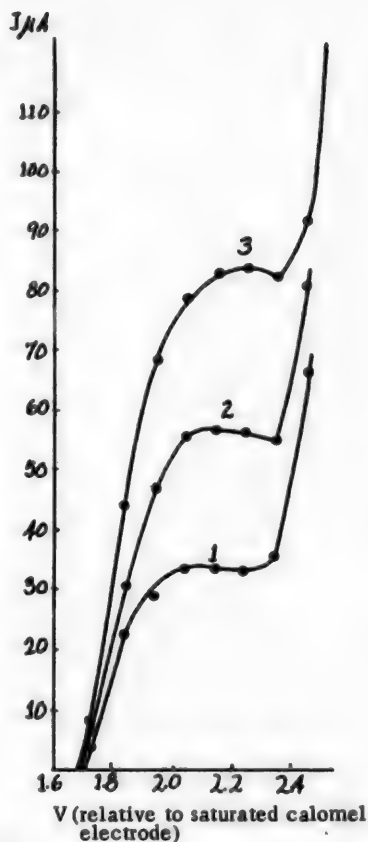


Fig. 2. Methyl acrylate polarograms. 1) $c = 15$ mmol/l; 2) $c = 30$ mmol/l; 3) $c = 45$ mmol/l. Background electrolyte $(\text{CH}_3)_4\text{NI}$ ($c = 0.1$ M in 50% $\text{C}_2\text{H}_5\text{OH}$).

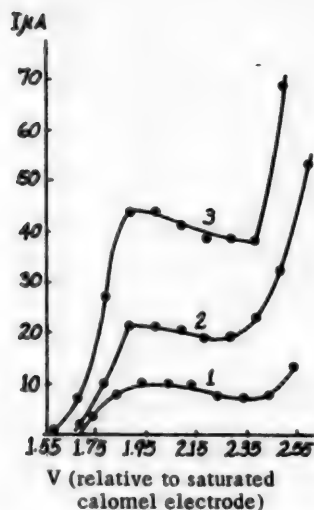


Fig. 3. Methacrylic acid polarograms. 1) $c = 10$ mmol/l; 2) $c = 15$ mmol/l; 3) $c = 30$ mmol/l. Background electrolyte $(\text{CH}_3)_4\text{NI}$ ($c = 0.1$ M in 50% $\text{C}_2\text{H}_5\text{OH}$).

grams in which gelatin was used, the authors came to the conclusion that by addition of gelatin they could bring the effect of the velocity of tangential movement of the mercury drop in the solution layer at the electrode to approximately zero.

The polarographic data obtained are given in Table 2 and in Figs. 2-7. It follows from their examination that the diffusion current values are in direct relation to the increase in concentration of ether.

The $E_{1/2}$ values were found from the polarogram by graphical means at $i_d/2$, as well as being obtained from the equation for polarographic wave

$$E = E_{1/2} - \frac{RT}{nF} \ln \frac{i}{i_d - i}$$

if $\log \frac{i}{i_d - i}$ is expressed graphically as a function of E at the value $\log \frac{i}{i_d - i} = 0$.

The number of electrons, \underline{n} , participating in the electrode process is determined as the product of the gradient angle tangent to the resulting straight line on RT/F . The value, \underline{n} , in the case of methylmethacrylate was found equal to 0.43, and for the methacrylic acid, 0.58, methyl methacrylate being 0.73, and butyl methacrylate 0.70.

Since the \underline{n} values found are fractional numbers, then for the given case, \underline{n} , there is found to be an apparent consumption of electrons. The theoretically expected \underline{n} value for the specific processes in the case of reversibility is equal to 2. Thus it can be considered that the reduction processes for the enumerated ethers at the dropping mercury electrode are irreversible.

In addition, the \underline{n} value was determined according to the Ilkovich equation $I = 605 \cdot m^{2/3} \cdot t^{1/6} \cdot D^{1/2} \cdot n \cdot c$. The diffusion coefficients for the polarographed ethers were calculated approximately, beforehand, according to

TABLE 2

Polarographic Data

Formula	Concentration, c (mmol/l)	Diffusion current, i_d (μ A)	i_d/c μ A · l mmol	Half-wave potential	
				at $i_d/2$	from the wave equation
$\text{CH}_2=\text{CH}-\text{C} \begin{array}{l} \text{O} \\ \parallel \\ \text{OCH}_3 \end{array}$	5	11.5	2.3	1.82	1.82
	10	23.5	2.35	1.82	
	15	33.6	2.24	1.82	
	15	33.5	2.23	1.79	
	25	54.5	2.18	1.83	
	30	57.5	1.91	1.83	
	35	76.5	2.19	1.81	
	45	84.5	1.88	1.83	
		Average	2.16	1.82	
$\text{CH}_2=\text{C} \begin{array}{l} \text{O} \\ \parallel \\ \text{OH} \end{array} \begin{array}{l} \text{CH}_3 \\ \end{array}$	10	10.5	1.05	1.74	1.76
	15	16.5	1.08	1.79	
	15	17.0	1.13	1.76	
	20	23.7	1.18	1.78	
	25	30.0	1.20	1.77	
	30	39.0	1.30	1.71	
	30	37.0	1.23	1.74	
	40	50.5	1.26	1.72	
		Average	1.18	1.76	
$\text{CH}_2=\text{C} \begin{array}{l} \text{O} \\ \parallel \\ \text{OCH}_3 \end{array} \begin{array}{l} \text{CH}_3 \\ \end{array}$	10	23.6	2.36	1.91	1.90
	15	36.5	2.43	1.90	
	20	44.5	2.22	1.90	
	30	68.0	2.27	1.95	
	40	86.5	2.16	1.92	
	45	102.0	2.27	1.88	
		Average	2.28	1.91	
$\text{CH}_2=\text{C} \begin{array}{l} \text{O} \\ \parallel \\ \text{OC}_4\text{H}_9 \end{array} \begin{array}{l} \text{CH}_3 \\ \end{array}$	10	20.5	2.05	1.91	1.925
	15	30.2	2.01	1.90	
	20	41.0	2.05	1.92	
	20	43.0	2.15	1.92	
	25	52.5	2.10	1.93	
	30	58.0	1.95	1.91	
	40	83.0	2.07	1.93	
	40	78.0	1.95	1.94	
	45	90.0	2.00	1.93	
		Average	2.03	1.92	

the formula composed on the basis of the Stokes-Einstein equation for spherical molecules at infinite dilution in aqueous solutions:

$$D = \frac{3.32 \cdot 10^{-5}}{(V_m)^{1/3}} \text{ cm}^2 \text{ sec}^{-1}$$

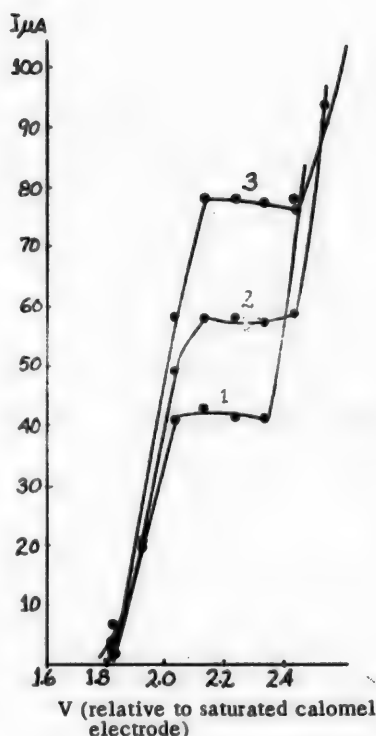


Fig. 4. Butyl methacrylate polarograms. 1) $c = 20$ mmol/l; 2) $c = 30$ mmol/l; 3) $c = 40$ mmol/l. Background electrolyte $(\text{CH}_3)_4\text{NI}$ ($c = 0.1$ m in 50% $\text{C}_2\text{H}_5\text{OH}$).

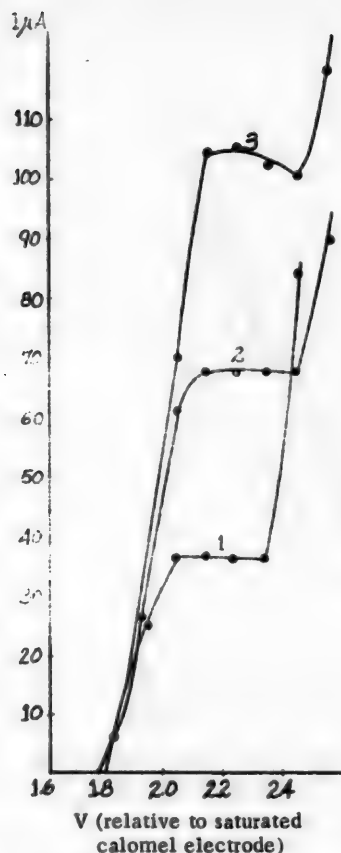


Fig. 5. Methyl methacrylate polarograms. 1) $c = 15$ mmol/l; 2) $c = 30$ mmol/l; 3) $c = 45$ mmol/l. Background electrolyte $(\text{CH}_3)_4\text{NI}$ ($c = 0.1$ m in 50% $\text{C}_2\text{H}_5\text{OH}$).

where D is the diffusion coefficient, $V_m = \frac{M}{d}$ is the apparent molecular volume of the substance in the solid state, M is the molecular weight, and d is the density [8].

Thus the values $D = 0.741 \cdot 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$ for methyl acrylate, $D = 0.755 \cdot 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$ for methacrylic acid, and $D = 0.69 \cdot 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$ for methyl methacrylate were found.

The n value was determined by substituting into the Ilkovic equation the values found for diffusion current at one concentration or another, the value $m^{2/3} \cdot t^{1/6}$ for the capillary constant, and the diffusion coefficient value, calculated according to the indicated method. For methyl acrylate the diffusion current value was $I_D = \frac{2.20}{0.956} = 2.26$.

Hence, the value $n = \frac{I_D}{605 \cdot D^{1/2}} = 1.39$. For methacrylic acid, $I_D = \frac{1.18}{0.956} = 1.13$ and $n = \frac{1.13}{1.664} = 0.68$. For methyl methacrylate, $I_D = \frac{2.38}{1.543} = 1.54$ and $n = \frac{1.54}{1.591} = 0.96$. The fractional n values found for those ethers polarographed by the authors in the manner indicated, being different from the expected value of 2, once more indicate an irreversibility of reactions at the dropping mercury electrode.

The authors calculated diffusion coefficient values also on the basis of the experimental data obtained for diffusion current, by considering that the electron number required for reducing 1 mole of substances should be equal to 2. It follows from the Ilkovic equation that

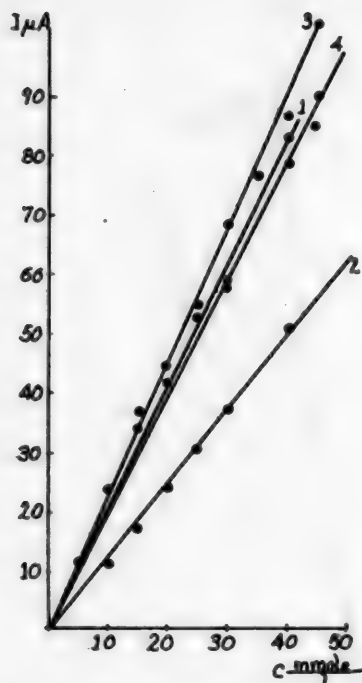


Fig. 6. Standard straight lines. 1) Methyl acrylate; 2) methacrylic acid; 3) methyl methacrylate; 4) butyl methacrylate.

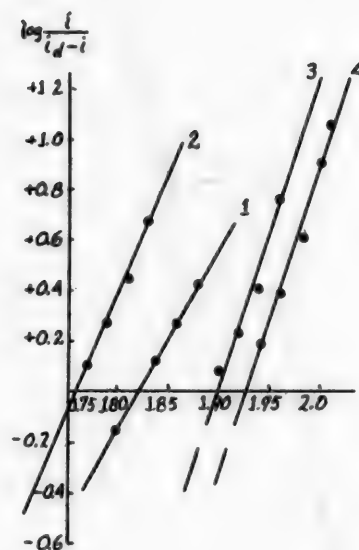


Fig. 7. Relation of $\log \frac{1}{i_d - i}$ to E. 1) Methyl acrylate; 2) methacrylic acid; 3) methyl methacrylate; 4) butyl methacrylate.

$$D = \left(\frac{I_D}{605 \cdot n} \right)^2 \text{ cm}^2 \text{ sec}^{-1}.$$

Thus for methyl acrylate $D = \left(\frac{2.26}{605 \cdot 2} \right)^2 = 0.35 \cdot 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$; for methacrylic acid $D = \left(\frac{1.13}{605 \cdot 2} \right)^2 = 0.085 \cdot 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$; for methyl methacrylate $D = \left(\frac{2.38}{605 \cdot 2} \right)^2 = 0.38 \cdot 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$; and for butyl methacrylate $D = \left(\frac{2.12}{605 \cdot 2} \right)^2 = 0.31 \cdot 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$.

EVALUATION OF RESULTS

From data obtained by the authors on polarographing the esters of acrylic and of methacrylic acid, as well as the free methacrylic acid, it follows that reduction occurs at the dropping mercury electrode in the presence of a conjugated double bond for the substance in question; without this, reduction does not occur.

Laitinen and Wawzonek [7] have studied a large number of unsaturated hydrocarbons, phenyl substituted olefins and acetylenes, as well as aromatic polycyclic hydrocarbons, and have determined that isolated ethylenic and acetylenic bonds are not reduced at the dropping mercury electrode; however, double bonds conjugated with carboxyl groups, or which are present in heterocyclic compounds, analogous to pyridine or quinoline, can be reduced. Electroreduction at the dropping mercury electrode of compounds with two conjugated double bonds, in particular of esters, has been studied by Meyman and Shubenko. Korshunov and Vodzinsky [8] and a number of other authors have studied the polarographic reduction of ketones with conjugated bonds. The possibility of electroreduction at the dropping mercury electrode of unsaturated compounds with conjugated double bonds in their molecules has also been confirmed by the results of the present authors.

The resulting half-wave potentials indicate great ease in electroreduction of methacrylic acid at the dropping mercury electrode, followed next by methyl acrylate, methyl methacrylate and butyl methacrylate; reduction of these latter two esters occurs under comparable conditions (see Table 2).

Half-wave potentials obtained graphically by the authors from polarograms (at $i_d/2$) coincide well with half-wave potentials obtained from the wave equation $\left(\text{at } \log \frac{1}{i_d - 1} = 0\right)$ which indicates applicability of this equation for expressing the basic electrode process as investigated.

Standard straight lines were constructed on the basis of resulting data from diffusion current values, from examination of which it follows that the increase in diffusion current of substances investigated is directly proportional to the increase in their concentration. The diffusion current constants $\frac{i_d}{\text{cm}^2 \sqrt{s} \sqrt{t}}$ for methacrylic acid, methyl acrylate, methyl and butyl methacrylates were calculated, respectively, as equal to: 1.13, 2.26, 2.38 and $2.12 \frac{\mu\text{A} \cdot 1}{\text{mmol}}$.

The function found for the diffusion current versus concentration can be used to study the polymerization kinetics of the above-named compounds, as well as for other processes in which these substances are involved.

From a comparison of data published in the literature on half-wave potentials, diffusion current constants, and diffusion coefficients values, for methyl methacrylate (2.0, 1.95 V; $1.91, 2.9 \frac{\mu\text{A} \cdot 1}{\text{mmol}}$; $0.25 \cdot 10^{-5}, 0.573 \cdot 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$) and butyl methacrylate (2.0 V; $2.8 \frac{\mu\text{A} \cdot 1}{\text{mmol}}$; $0.533 \cdot 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$) with the data obtained by the authors for methyl methacrylate (1.90 V; $2.38 \frac{\mu\text{A} \cdot 1}{\text{mmol}}$; $0.38 \cdot 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$) and butyl methacrylate (1.92 V; $2.12 \frac{\mu\text{A} \cdot 1}{\text{mmol}}$; $0.38 \cdot 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$), it follows that the half-wave potentials, diffusion current constants and diffusion coefficient values obtained by the authors occupy an intermediate phase as compared with the data published in the literature.

SUMMARY

1. Vinyl ethers which do not possess conjugated bonds in the molecule, in $(\text{CH}_3)_4\text{NI}$ solution in 75% $\text{C}_2\text{H}_5\text{OH}$, or in weakly alkaline or acid medium, do not reduce at the dropping mercury electrode.
2. Methyl acrylate, methacrylic acid, methyl methacrylate and butyl methacrylate containing conjugated bonds in the molecule, in a background electrolyte of $(\text{CH}_3)_4\text{NI}$ in 50% $\text{C}_2\text{H}_5\text{OH}$ are reduced polarographically and can be determined quantitatively.

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A COMPARISON OF INVESTIGATIONAL METHODS OF COMPLEX-FORMING SYSTEMS IN ORGANIC CHEMISTRY

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In a number of investigations on the chemistry of complex organic compounds under the direction of one of the authors, various methods for detection and determination of the composition of complex compounds have been used. Results of a number of works make it possible to summarize the findings which pertain to a comparison of these methods.

I. Preparative methods, i.e., direct isolation of the complexes, and their subsequent analysis. It is possible to obtain relatively stable compounds (for example, quinhedrone, naphthalene picrate) in crystalline form by direct mixing of the component parts of the complex. At times the complex precipitates upon cooling the hot solution of one substance in the other, as for example hydroquinone and pyridine. In some cases good results are obtained by melting a mixture of the substances under investigation. Thus, the authors prepared, for example, a complex of phenol with α -aminopyridine.

To obtain unstable complexes, which at times could not be detected even by physico-chemical means, the authors successfully applied the reaction of vapors of the more volatile constituent upon crystals of the less volatile constituent. This method, popular in inorganic chemistry, as for example in the preparation of ammoniacs, was first used by the authors during an investigation of complex-forming systems containing quinone. Thus, 16 compounds of quinone with phenols were prepared, whereas it was not possible to prepare or to identify the very unstable complexes of trichlorophenol, tribromophenol, m-cresol or 1,2,4-tribromocresol by any method.

There is described in the present work the synthesis of a series of nitrophenol complexes with amines. The method has been extended by the authors to compounds of low volatility at normal temperature. They were successfully reacted by heating. Finally, for qualitative detection of the complexes, if the latter possessed a characteristic color, grinding of the solid substances sufficed.

The method of preparing complexes based upon reaction of crystals with vapors is not suitable for substances with too low a melting point (though of course it can be extended to those substances if reaction is carried out with considerable cooling). Moreover, melting of the crystals is sometimes observed as the result of formation of a low-melting eutectic of the complex with one of the complex components [1]. In such cases, complex formation can be qualitatively determined by coloration, though the composition of the complex cannot be determined.

Finally, experiments with quinone have indicated that at times reaction between crystals and vapors does not occur in those compounds which form a definite complex in solution. This phenomenon was observed with anthracene, phenanthrene, acenaphthene and dibenzylsulfide. For the compounds enumerated, complex formation with quinone was proved colorimetrically, and others by thermal analysis. Apparently the quinone molecules cannot penetrate into the crystalline lattices of other substances.

II. Methods of Physico-Chemical Analysis, of which the Following were used by the Authors

1) The classical method of thermal analysis. Complex formation of phenols, carboxylic acids, organic sulfides, nitro compounds, amines, and amides was studied in various combinations. New complexes were found, but on the whole the method was not very sensitive. Instability of many compounds to heat was evident.

2) Colorimetric analysis. This was introduced for the first time into the chemistry of organic complexes by Ostromyslensky [2]. The method was applied by the authors in a rough form, using a Dubosq colorimeter. As indicated by complex formation of nitro compounds with amines, which was studied in particular, colorimetric measurement led to positive results for many systems where the melting diagrams did not exhibit chemical interaction. In experiments with nitro compounds and amines, this phenomenon occurred in 6 cases, but in only three systems (α -nitronaphthalene-aniline, m-dinitrobenzene-aniline, m-dinitrobenzene-benzidine) did both methods give positive results, as well as indicate identical compositions for the complexes [1].

3) The electrochemical method. This method was developed at the Tomsk Polytechnic Institute organic chemistry laboratory, based upon a determination of current density in a closed circuit, where the source of energy was the reaction of the compound under investigation, or of the mixture with metal [3]. Measurement was carried out by means of a sensitive galvanometer with high resistance. The current density values read on the galvanometer depend upon the EMF appearing during reaction, and upon electroconductivity of the system under study. Polarization also exerts an influence. Experiments have indicated, however, that during investigation of organic compounds the method in question can give a good characterization of reactivity with respect to metals. In studying complex formation, the method was found to be very sensitive, if, of course, reaction occurs with metals [4].

More than 200 systems were investigated, and more than 100 complexes determined, many of which failed to be detected by the melting diagrams. Some complexes were then isolated, and their compositions determined entirely, or almost so, for those compositions corresponding to maximum deviation of the galvanometer needle. It also became apparent that the value shown by the millivoltmeter characterized the molecular compound better than did the electroconductivity of the mixture.

In the experimental part of the authors' work, complex formation between phenols and the aromatic and heterocyclic amines is described. Investigation was carried out by the preparative procedure in various modifications, and by two physico-chemical methods of analysis: fusion diagrams, and electrochemically, according to Tronov and Kulev. The authors attempted to apply both methods to the same systems.

Eight complexes were isolated by the preparative method in various modifications. The principal complex formers were benzidine (3 complexes), α -aminopyridine (3 complexes), and β -naphthylamine (2 complexes). Composition of one benzidine and of both naphthylamine complexes corresponded to a ratio of 1 : 1 for phenolic hydroxyl : amino group, i.e., complex formation in this case should proceed according to the standard acid-amine manner. In one complex a polyhydroxy phenol reacted with benzidine, but not with all of the hydroxyls. Trichlorophenol possessed an unusual composition with benzidine, in which two hydroxyls were assigned to one amino group. Composition of the phenols with aminopyridine compounds was variable. Aminopyridine possesses two nitrogens, and either one or both can enter into reaction. Complexes are possible between aminopyridine and nitrophenols, and bonds of amino nitrogen with hydroxyl or with nitro groups, as indicated by retention of a light-yellow color in the former and deepening of the color in the latter.

TABLE

No.	System	By the Tronov-Kulev electrochemical method	Complexes, found			
			by thermal method of analysis	by viscosity	by electroconductivity	by preparatory method
1	Phenol-aniline	1:1 2:1	1:1 [8]	2:1 [8]	1:1 [11], 1:2 [10]	1:1 [12], 2:1 [13]
2	Phenol-dimethylaniline	—	— [9]	s-shaped curve		
3	Phenol- α -naphthylamine	1:1 4:1	1:1 [16]			1:1 [18]
4	Phenol-pyridine	1:1	1:1, 2:1 [8]			1:1, 2:1 [17]
5	Phenol- α -aminopyridine	2:1	1:1			1:1
6	o-Chlorophenol-aniline	1:1	1:1 [14]			
7	o-Chlorophenol-dimethylaniline	—	1:1 [14]			
8	o-Chlorophenol-pyridine	2:3, 1:1	1:1 [14]	4:1		
9	o-Chlorophenol- α -aminopyridine	1:1, 2:1				2:1
10	o-Chlorophenol-quinoline	1:1, 3:2	1:1 [14]			
11	o-Nitrophenol- α -aminopyridine	1:1	—			
12	α -Naphthol-pyridine	1:1	Does not crystallize, vitreous mass.	2:1 [19]	2:1 [19]	
13	α -Naphthol-quinoline	1:1	1:1, 1:2 [15]	1:1 [15]	1:1 [15]	
14	β -Naphthol-pyridine	2:3, 2:1		2:1 [19]	2:1 [19]	
15	β -Naphthol-quinoline	1:1, 2:1	1:1, 2:1 [15]	2:1 [15]	2:1 [15]	

Note: First number = number of phenol molecules; second number = number of amine molecules; dash = no interaction.

It is to be regretted that results obtained by the preparative investigation method could not always be compared with the physico-chemical method of analysis, and especially with the electrochemical analysis according to Tronov and Kulev, since the last method was of particular interest to the authors. Electrochemical analysis required the use of solvents in which some of the phenols are poorly soluble; in the table, therefore, in which a comparison of methods is made, only a few investigational results are given. For the phenols and amines enumerated in the table, complete data on the investigation of these compounds by the method of Tronov and Kulev, and a considerable amount of data by the thermal method of analysis are available. Data found in the literature for the electroconductivity and viscosity of these same systems are also included.

The table indicates a somewhat higher sensitivity for the Tronov-Kulev method. If 12 systems be taken, in which this last method and thermal analysis are applied, there then will be found electrochemically 15 complexes, and by thermal analysis, 13 complexes. From their compositions, 9 coinciding complexes were found, 6 were found by electrochemical analysis only, and 4 thermally; in one case (phenol-dimethylaniline) both methods led to negative results. Measurements of viscosity and of electroconductivity frequently yielded the same results as with the preceding two methods, but at times indicated a fewer number of complexes, and at times also made possible the detection of new complexes. On the whole, however, comparison here remains quite fragmentary.

In general, none of the methods for investigating complex formation can be considered to be favored over all the others. Each method has its area of application, which is defined by the properties of all of the compounds studied. The colorimetric method is very sensitive, but applicable only in those cases where upon formation of a complex there is an appearance of, or a change in, coloration. In the electroconductivity determination there is the requirement that the system not possess a very low electroconductivity. The electrochemical method, as developed in the Soviet Union, is based upon reaction with metals, but not all organic substances are capable of reaction with metals; furthermore, the likelihood of obtaining good results is related to the solubilities of the compounds used in the solvents required for the work.

Finally, there should be taken into account the fact that the formation of any complex may have differing influences upon indices determined by physico-chemical analysis; so, at times in the same system, one method indicates a complex of a given composition, the formation of which has a more pronounced effect on that specific property of the substances, while the characterizing curve obtained by use of another physical index shows particular points at other places. So, for a complete study of any one system with respect to formation of complexes, several methods should be used.

EXPERIMENTAL

I. Isolation of Complexes from Solutions and from Melts

1. Phenol- α -aminopyridine. The complex crystallized slowly from the melt of equimolecular amounts of the starting substances. Large elongated platelets, white in color, washed with benzene, melted at 21-22°.

0.2265 g sub.: 23.60 ml 0.1 N H_2SO_4 . 0.2520 g sub.: 25.59 ml 0.1 N H_2SO_4 . Found %: N 14.64, 14.28 (according to the Kjeldahl modified method [5]). $C_6H_5OH \cdot C_5H_4N(NH_2)$. Calculated %: N 14.85.

2. o-Chlorophenol- α -aminopyridine. The compound was obtained in an identical fashion. The white precipitate which formed, possessed a m.p. of 42-43.5° after 2 washings with small amounts of benzene. Complex volatile in air.

0.1902 g sub.: 0.1640 g AgCl. 0.1932 g sub.: 0.1632 g AgCl. 0.2454 g sub.: 12.10 ml 0.1 N H_2SO_4 . 0.2600 g sub.: 13.34 ml 0.1 N H_2SO_4 . Found %: Cl 21.60, 20.94; N 6.90, 7.18. $2C_6H_4ClOH \cdot C_5H_4N(NH_2)$. Calculated %: Cl 20.23; N 7.97.

3. p-Nitrophenol- α -aminopyridine. Upon mixing the benzene solution, fine yellow crystals precipitated, which, after washing with benzene and drying, had a m.p. of 89-90°. The complex was stable in air.

0.1366 g sub.: 14.70 ml 0.1 N H_2SO_4 . 0.1336 g sub.: 14.80 ml 0.1 N H_2SO_4 . Found %: N 15.06, 15.50. $[C_6H_4NO_2OH]_2 \cdot C_5H_4N(NH_2)$. Calculated %: N 15.04.

4. Pyrogallol-benzidine. Formed during mixing of benzene solutions at a ratio of 1:1 for pyrogallol to benzidine. White, elongated, hexagonal platelets, with m.p. 143-144.5°.

0.4110 g sub.: 26.83 ml 0.1 N H_2SO_4 . 0.4106 g sub.: 27.20 ml 0.1 N H_2SO_4 . Found %: N 9.11, 9.29. $C_6H_3(OH)_3 \cdot (C_6H_4NH_2)_2$. Calculated %: N 9.00.

The molecular ratio of initial substance at 2:1 led to formation of the same compound, and some crystals of different form, composition not characterized. The melting diagram for the system had 3 maxima, corresponding to the compositions 1:1, 2:1 and 3:2 (the first number indicating number of pyrogallol molecules).

5. Phloroglucinol-benzidine. The complex precipitated from aqueous solution. White, rhomboidal platelets with m.p. 164-167°. Readily soluble in alcohol and acetone, less so in ether and poorly so in cold water.

0.4096 g sub.: 30.55 ml 0.1 N H_2SO_4 . 0.4130 g sub.: 31.53 ml 0.1 N H_2SO_4 . Found %: N 10.45, 10.68. $2\text{C}_6\text{H}_3(\text{OH})_3 \cdot 3(\text{C}_6\text{H}_4\text{NH}_2)_2$. Calculated %: N 10.44.

6. 2,4,6-Trichlorophenol-benzidine. The purest complex resulted from a benzene solution at a molecular ratio of 6:1 for trichlorophenol to benzidine. Needle crystals, with m.p. 99-100°. Readily soluble in chloroform, alcohol, ether. It lost trichlorophenol to the air slowly.

0.1678 g sub.: 3.68 ml 0.1 N H_2SO_4 . 0.1430 g sub.: 3.00 ml 0.1 N H_2SO_4 . 0.1026 g sub.: 0.1793 g AgCl. 0.0794 g sub.: 0.1378 g AgCl. Found %: N 3.07, 2.93; Cl 43.30, 43.54. $4\text{C}_6\text{H}_2(\text{OH})\text{Cl}_3 \cdot (\text{C}_6\text{H}_4\text{NH}_2)_2$. Calculated %: N 2.87; Cl 43.75.

7. 2,4-Dichlorophenol- α -naphthylamine. The complex resulted upon mixing saturated benzene solutions together in equimolecular amounts. Needle crystals, m.p. 72-73°. Soluble in benzene, ether and chloroform. Decomposed by hot water. Gradually lost dichlorophenol to the air.

0.1868 g sub.: 6.60 ml 0.1 N H_2SO_4 . 0.2144 g sub.: 7.60 ml 0.1 N H_2SO_4 . 0.1618 g sub.: 0.1500 g AgCl. 0.1914 g sub.: 0.1777 g AgCl. Found %: N 4.94, 4.96; Cl 22.92, 23.01. $\text{C}_6\text{H}_3(\text{OH})\text{Cl}_2 \cdot \text{C}_{10}\text{H}_7\text{NH}_2$. Calculated %: N 4.57; Cl 23.20.

8. 2,4,6-Trichlorophenol- β -naphthylamine. 0.02 mole of trichlorophenol was added, with stirring, to 0.02 mole of β -naphthylamine in 40 ml of benzene; complete dissolution of components was effected. After a half-hour, a flaky precipitate began to form. It was washed with benzene and dried at 50°; m.p. 94-96°. The complex was soluble in benzene, alcohol and chloroform. It lost trichlorophenol in the air.

0.4024 g sub.: 12.58 ml 0.1 N H_2SO_4 . 0.4012 g sub.: 12.12 ml 0.1 N H_2SO_4 . 0.1532 g sub.: 0.1922 g AgCl. 0.1486 g sub.: 0.1858 g AgCl. Found %: N 4.39, 4.22; Cl 31.03, 31.90. $\text{C}_6\text{H}_2(\text{OH})\text{Cl}_3 \cdot \text{C}_{10}\text{H}_7\text{NH}_2$. Calculated %: N 4.11; Cl 31.25.

II. Preparation of Complexes by Heterogeneous Reactions

The systems studied were those in which nitrophenol on the one hand, and amines of low volatility on the other, were used. Nitrophenols were particularly suited to the method in question since they produced bright-colored compounds, whose presence was easy to detect. For a majority of the systems first taken, the authors carried out the qualitative test by grinding the crystals. For the quantitative investigation, beakers containing the reacting components were placed in an apparatus consisting of small desiccator, placed in a thermostatic box, equipped with contact thermometer. After a specified interval, the beaker, with non-volatile substance, was weighed. Thus the reaction rate was determined, and in those cases where a crystalline product resulted, the weight gain could be determined as well as the composition of the complex. Complex formation was accelerated upon continuous stirring of the crystals.

1. 2,4-Dinitrophenol + α -aminopyridine. Reaction temperature was 50°. The resulting bright-red crystals melted at 154-155°, and after crystallization from chloroform, had a m.p. of 156-157°. Stable in air. Decomposed by acid and alkalis.

0.1530 g sub.: 22.15 ml 0.1 N H_2SO_4 . 0.1454 g sub.: 21.20 ml 0.1 N H_2SO_4 (according to the modified Kjeldahl method). Found %: N 20.26, 20.34. $\text{C}_6\text{H}_3(\text{NO}_2)_2\text{OH} \cdot \text{C}_5\text{H}_4\text{N}(\text{NH}_2)$. Calculated %: N 20.14.

The same data were obtained by the quantity of aminopyridine added (experiment continued until beaker with dinitrophenol reached constant weight), i.e., by the gain in weight: 0.5000 g of dinitrophenol gave 0.7567 g of complex; for a complex of the indicated composition, 0.7556 g is required, i.e., 100.14% of theory was obtained.

2. 2,5-Dinitrophenol + α -aminopyridine. Temperature 50°. The complex was in the form of carmine-red needles with m.p. 150°. After recrystallization from benzene, it melted at 151-152°. Stable in air. Decomposed by water and acids. Soluble in hot benzene or chloroform, with disappearance of the red color, but upon cooling, precipitated in the previous form.

0.1222 g sub.: 17.78 ml 0.1 N H_2SO_4 . 0.0840 g sub.: 15.94 ml 0.1 N H_2SO_4 . Found %: N 20.38, 19.90 (according to Kjeldahl). $\text{C}_6\text{H}_3(\text{NO}_2)_2\text{OH} \cdot \text{C}_5\text{H}_4\text{N}(\text{NH}_2)$. Calculated %: N 20.14.

0.500 g of dinitrophenol: weight of complex 0.7556 g. Calculated: 0.7556 g. Found: 99.86% of theory.

Upon stirring the complex with 2,4,6-trinitrophenol crystals, the color gradually changed to yellow as a result of aminopyridine picrate formation.

3. 2,6-Dinitrophenol + α -aminopyridine. Conditions the same. Orange needle crystals resulted with m.p. 198-198.5°. Recrystallized from benzene and chloroform. Decolorized by ethyl alcohol and sulfuric acid. Stable in air. As with preceding, slowly sublimed above 50°.

0.1100 g sub.: 16.00 ml 0.1 N H_2SO_4 . 0.1216 g sub.: 17.68 ml 0.1 N H_2SO_4 . Found %: N 20.36, 20.05 (according to Kjeldahl). $\text{C}_6\text{H}_3(\text{NO}_2)_2\text{OH} \cdot \text{C}_5\text{H}_4\text{N}(\text{NH}_2)$. Calculated %: N 20.14.

0.5000 g of dinitrophenol: 0.7532 g is the weight of complex. Calculated: 0.7558 g. Found: 99.68% of theory.

Color of the complex with trinitrophenol changed to yellow.

4. p-Nitrophenol + α -aminopyridine. Temperature was 50°. The substance melted during the reaction.

5. p-Nitrophenol + pyridine. The experimental temperature was 15-17°. Lemon-yellow crystals with m.p. 63-64° resulted, which is in accordance with the literature data [6].

0.5000 g of nitrophenol: 0.7929 g is the weight of the complex. $\text{C}_6\text{H}_4(\text{NO}_2)\text{OH} \cdot \text{C}_5\text{H}_5\text{N}$. Calculated: 0.7842 g. Found: 101.1% of theory.

6. 2,4-Dinitrophenol + pyridine. Temperature 15-17°. Light-orange crystals with m.p. 79-80° resulted. The complex, as with the preceding one, slowly lost pyridine.

0.5000 g of dinitrophenol: 0.7208 g is the weight of the complex. $\text{C}_6\text{H}_3(\text{NO}_2)_2\text{OH} \cdot \text{C}_5\text{H}_5\text{N}$. Calculated: 0.7158 g. Found: 100.69% of theory.

Upon mixing with aminopyridine, there gradually formed the complex already described of the latter with dinitrophenol.

7. 2,4-Dinitrophenol + α -aminopyridine. The experiment was carried out with continuous stirring of the crystals of reacting substances. Temperature was 50°. The mixture was analyzed from time to time by washing away the aminopyridine with carbon tetrachloride and drying the residue at 45° to constant weight. The complex, m.p. 153-155°, described earlier, resulted, but the reaction was 98% complete after 2.5 hours, while with the previous synthetic method it was continued for 28 days.

By the same method, 2,4-dinitrophenol was reacted with non-volatile amines: α -naphthylamine, β -naphthylamine, benzidine. The properties of the complexes coincided with the properties as described in the literature [7].

III. A Study of Complex Formation by the Thermal Analysis Method

The apparatus used for thermal analysis consisted of a test tube equipped with stirrer and calibrated thermometer, glass sleeve for uniform heating and cooling of the substance in the tube, and a glycerine bath. Calculations for the components was carried out in mol. %. Experiments were usually set up with ratios differing by 10% from each other. For some parts of the diagram, points were plotted more frequently.

The batches of substances taken were placed in the tube and melted. Then, with cooling and constant stirring of the melt, the temperature of the liquid mixture was determined every minute and especially the temperature for first appearance of crystals, and for eutectic crystallization. In the systems with α -aminopyridine, cooling was carried out with snow and cooling mixture. Supercooling was avoided by vigorous stirring and the use of seeders. Results obtained are given in Figs. 1, 2 and 3.

IV. A Study of Complex Formation by the Tronov-Kulev Electrochemical Method

The experiments were carried out in an apparatus as described by the authors of the method [3]. Its construction is given in Fig. 4, where (1) is a metallic cylinder with hard rubber sleeve; (2) is a platinum crucible; (3) is a hard rubber cover, tightly sealing the cylinder; (4) is a metal plug; (5) is a contact plate; (6) and (7) are the brass rod with pointed tip for sodium electrode; (8) is a glass socket; (9) is the mobile contact; (10) the

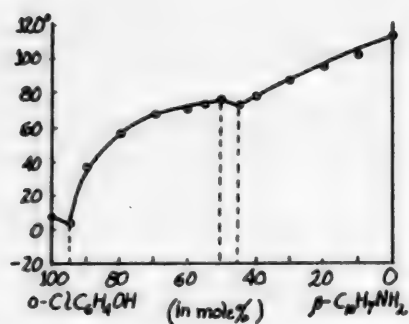


Fig. 1. o-Chlorophenol- β -naphthalene system.

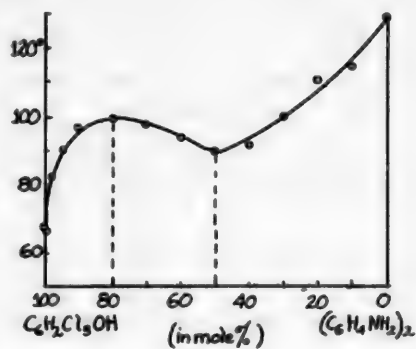


Fig. 2. Trichlorophenol-benzidine system.

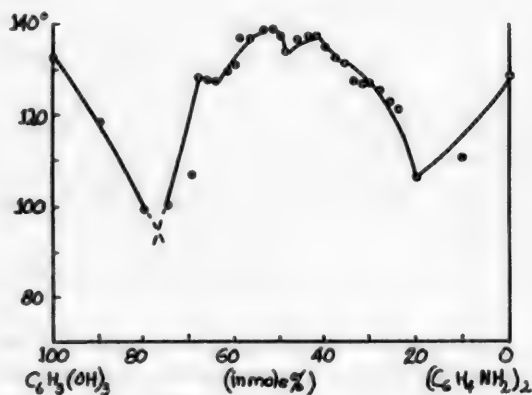


Fig. 3. Pyrogallol-benzidine system.

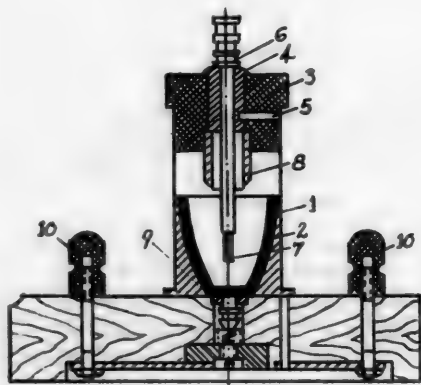


Fig. 4. Exaplanation in text.

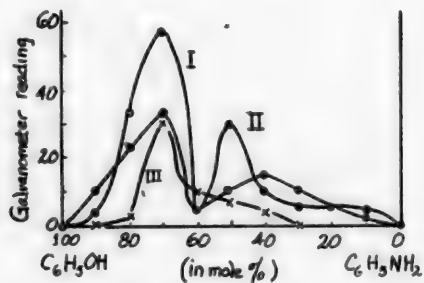


Fig. 5. Phenol-aniline system. I) Concentration 1:40 M; II) concentration 1:40 M, temperature 43°; III) concentration 1:80 M,

outlet plates for connection with galvanometer. The length of the glass sleeve was such that the pressed sodium electrode protruded only about $\frac{3}{4}$ of the way out of the socket, and the remaining portion was tightly sealed from access of liquid inside the socket.

The substances investigated, taken in specific molar ratios, were placed in the platinum crucible, and benz added to total volume of 6 ml. The crucible, which also served as one electrode, was lowered into the hard rubber socket of the metallic cylinder, from the bottom of which through an outlet (10) was attached the galvanometer. Then, by means of the ground end of the glass socket, fastened into the hard rubber cover, there served as

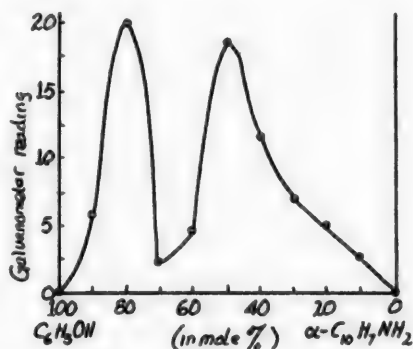


Fig. 6. Phenol- α -naphthylamine system.

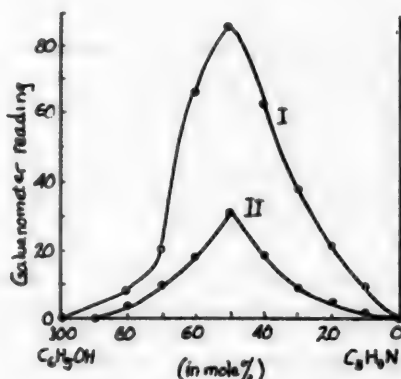


Fig. 7. Phenol-pyridine system. I) Concentration of 1:60 M; II) concentration of 1:80 M.

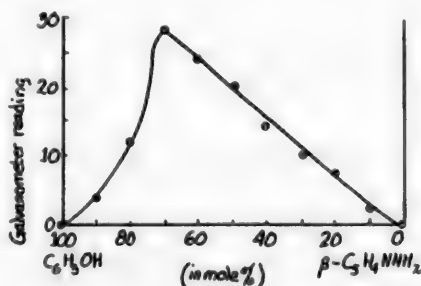


Fig. 8. Phenol- α -aminopyridine system.

the second electrode a small cylinder cut from sodium, 6 mm in diameter and 9 mm long, the cover being placed into cylinder (1). The sodium was pressed out into the liquid by a brass rod connected, through the plate (5), with the other galvanometer contact. At the same time, galvanometer readings were taken at specific time intervals: 30 sec, 1 min, 2 min, and so forth.

A galvanometer of the S-IV type from the Physics Institute of the Leningrad University was used, with a resistance of 2800 ohms, and a scale of 45 mV. For each ratio maximum, readings were taken on the galvanometer and curves plotted according to the data. From the character of the curves, conclusion

could be drawn as to the composition of the complexes being formed. As a rule, experiments were carried out at 15-17°, some other systems being studied at higher temperature and different concentrations.

The experimental results are presented in the table and in Figs. 5, 6, 7 and 8.

SUMMARY

1. A comparison of several methods of studying complex forming systems has been carried out. Systems composed of phenols and amines have been studied experimentally. Methods of investigation have been: direct isolation of the complexes, with chemical analysis of the latter and physico-chemical analysis.

2. Eight new complexes have been isolated and analyzed. During the preparation of the complexes, good results have been obtained by the method of heterogenic reactions. Crystals of non-volatile components of the system have reacted with vapors of the volatile component.

3. Of the various available physico-chemical methods, the methods of thermal analysis and of Tronov and Kulev's electrochemical procedure based upon determination of current density in a closed circuit where the energy source is the reaction of the substance studied with metal, have been utilized. This latter method has been found to be somewhat more sensitive.

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COMPOUNDS OF ZINC HALIDE WITH NICOTINE*

S. F. Babak and I. A. Kondrashov

In the preceding works [1, 2], the authors have demonstrated that nicotine forms two types of compounds: $\text{HgX}_2 \cdot \text{C}_{10}\text{H}_{14}\text{N}_2$ and $\text{HgX}_2 \cdot \text{C}_{10}\text{H}_{14}\text{N}_2 \cdot 2\text{HX}$, with mercury halides. Nicotine forms analogous type compounds with cupric chloride and cupric bromide, as well as of another composition which is apparently affected both by the nature of the metal and by the conditions of the reaction course.

In the present work the synthesis, composition, and properties, of compounds of nicotine with zinc halides are described. With respect to compounds of nicotine with zinc halides, the following are known: $\text{ZnI}_2 \cdot \text{C}_{10}\text{H}_{14}\text{N}_2$, $\text{ZnCl}_2 \cdot \text{C}_{10}\text{H}_{14}\text{N}_2 \cdot 2\text{HCl} \cdot \text{H}_2\text{O}$ and $\text{ZnCl}_2 \cdot \text{C}_{10}\text{H}_{14}\text{N}_2 \cdot 2\text{HCl} \cdot 4\text{H}_2\text{O}$ [3].

The interaction of nicotine with zinc halides has been studied in acetone by the authors, and in aqueous solutions in the presence of the acids; here three compounds have been found: $\text{ZnX}_2 \cdot 2\text{C}_{10}\text{H}_{14}\text{N}_2$, $\text{ZnX}_2 \cdot \text{C}_{10}\text{H}_{14}\text{N}_2 \cdot \text{HX}$ and $\text{ZnX}_2 \cdot \text{C}_{10}\text{H}_{14}\text{N}_2 \cdot 2\text{HX}$. Compounds of the first type result from mixing of anhydrous acetone solutions of nicotine and of zinc halides in stoichiometric ratios. Compounds of the second type are formed upon mixing aqueous solutions in equimolecular quantities, as they enter into the composition of the components. The third type of compound results upon mixing zinc halides and nicotine in a 1:1 ratio and in a highly acid aqueous medium of the corresponding hydrogen halides. Compounds of the first and third types result with a small excess of nicotine.

The nicotine boiled at 111-112° (6 mm), $d_{25} 1.0068$, $\eta_{25} 3.8942$. Dry acetone was used, ZnCl_2 — chemically pure, ZnBr_2 and ZnI_2 were prepared by reacting ZnO with hydrobromic and hydriodic acids. HCl was purified by distillation. HBr and HI were prepared and purified by standard methods. Zinc was determined by the weight method as a zinc sulfate form of the zinc oxide; halides were determined according to Volhard as silver halides, nicotine was titrated with sulfuric acid in the presence of methyl red, after distilling from alkaline solution with steam.

$\text{ZnCl}_2 \cdot 2\text{C}_{10}\text{H}_{14}\text{N}_2$. After mixing acetone solutions of zinc chloride and nicotine, white crystals precipitated from solution after the second day. The crystals were filtered off, washed with acetone and dried in a vacuum desiccator. Yield was 85%. The compound melted with decomposition at 138-140°.

$\text{ZnBr}_2 \cdot 2\text{C}_{10}\text{H}_{14}\text{N}_2$. Upon mixing acetone solutions of zinc bromide and of nicotine, white fine, crystals precipitated from solution immediately. The crystals were filtered off, washed with ether and dried in a desiccator. The resulting compound melted at 148-150° with decomposition. Yield was 87%.

$\text{ZnI}_2 \cdot 2\text{C}_{10}\text{H}_{14}\text{N}_2$. The preparational method for this compound was similar to the preceding. The white, crystalline substance melted with decomposition at 125-126°. Yield was 91%.

$\text{ZnCl}_2 \cdot \text{C}_{10}\text{H}_{14}\text{N}_2 \cdot \text{HCl}$. The compound resulted from mixing aqueous solutions consisting of equimolecular amounts of zinc chloride, hydrochloric acid and nicotine. Fine, white crystals immediately formed in solution. The crystals were filtered off by suction, washed with water, and dried. Melted with decomposition at 241-246°. Yield was 89%.

$\text{ZnBr}_2 \cdot \text{C}_{10}\text{H}_{14}\text{N}_2 \cdot \text{HBr}$. Prepared in the same manner as preceding. The white crystals melted with decomposition at 257-260°. Yield was 90%.

$\text{ZnBr}_2 \cdot \text{C}_{10}\text{H}_{14}\text{N}_2 \cdot 2\text{HBr}$. The compound resulted on mixing equimolecular amounts of aqueous solutions of zinc bromide and nicotine in the presence of a large amount of hydrobromic acid. The solution was concentrated with charcoal and filtered while hot. Upon cooling, white crystals precipitated from the filtrate, which were separated on a Schott filter, washed with cold water and dried in a desiccator. The compound melted with decomposition at 214-216°, Yield was about 77%.

* N. Kalustova participated in the experimental part.

$\text{ZnI}_2 \cdot \text{C}_{10}\text{H}_{14}\text{N}_2 \cdot 2\text{HI}$. The compound was formed by mixing aqueous solutions of zinc iodide and nicotine in 1:1 ratio in the presence of a large amount of hydriodic acid. There precipitated immediately from solution slightly-yellow crystals, which were separated and washed with a small amount of cold water; with such procedure they became white, and again yellow when stored in a desiccator due to their partial decomposition by separation of iodine. Melting with decomposition at 237-238°. Yield about 30%.

TABLE

Analytical Results for Compounds Obtained

No.	Compound	Melting point	Nicotine (%)		Zinc (%)		Halide (%)	
			found (average)	calculated	found (average)	calculated	found (average)	calculated
1	$\text{ZnCl}_2 \cdot 2\text{C}_{10}\text{H}_{14}\text{N}_2$	138-140°	70.08	70.41	13.64	13.38	15.66	15.39
2	$\text{ZnBr}_2 \cdot 2\text{C}_{10}\text{H}_{14}\text{N}_2$	148-150	59.10	59.01	11.61	11.89	29.13	29.09
3	$\text{ZnI}_2 \cdot 2\text{C}_{10}\text{H}_{14}\text{N}_2$	125-126	50.42	50.38	10.11	10.16	40.08	39.44
4	$\text{ZnCl}_2 \cdot \text{C}_{10}\text{H}_{14}\text{N}_2 \cdot \text{HCl}$	241-246	48.48	48.55	19.46	19.52	31.14	31.76
5	$\text{ZnBr}_2 \cdot \text{C}_{10}\text{H}_{14}\text{N}_2 \cdot \text{HBr}$	257-260	34.53	34.62	13.82	13.96	51.22	51.19
6	$\text{ZnBr}_2 \cdot \text{C}_{10}\text{H}_{14}\text{N}_2 \cdot 2\text{HBr}$	214-216	29.54	29.52	11.82	11.89	57.94	58.17
7	$\text{ZnI}_2 \cdot \text{C}_{10}\text{H}_{14}\text{N}_2 \cdot 2\text{HI}$	237-238	21.41	21.72	8.68	8.86	69.01	68.86

Compounds of zinc halide with nicotine containing no acid in their composition are poorly soluble in water. $\text{ZnCl}_2 \cdot 2\text{C}_{10}\text{H}_{14}\text{N}_2$ dissolves in methyl and ethyl alcohols; $\text{ZnBr}_2 \cdot 2\text{C}_{10}\text{H}_{14}\text{N}_2$ dissolves in methyl but does not dissolve in ethyl alcohol. Both are poorly soluble in ether and acetone. $\text{ZnI}_2 \cdot 2\text{C}_{10}\text{H}_{14}\text{N}_2$ does not dissolve in the indicated solvents. Acid-containing compounds of zinc halide with nicotine are soluble in water and insoluble in ether, acetone, methyl and ethyl alcohols. All compounds described dissolve readily in hydrobromic, hydrochloric and hydriodic acids, as well as in nitric acid.

SUMMARY

Crystalline compounds of nicotine with zinc halides have been prepared as follows: $\text{ZnCl}_2 \cdot 2\text{C}_{10}\text{H}_{14}\text{N}_2$, $\text{ZnBr}_2 \cdot 2\text{C}_{10}\text{H}_{14}\text{N}_2$, $\text{ZnI}_2 \cdot 2\text{C}_{10}\text{H}_{14}\text{N}_2$, $\text{ZnCl}_2 \cdot \text{C}_{10}\text{H}_{14}\text{N}_2 \cdot \text{HCl}$, $\text{ZnBr}_2 \cdot \text{C}_{10}\text{H}_{14}\text{N}_2 \cdot \text{HBr}$, $\text{ZnBr}_2 \cdot \text{C}_{10}\text{H}_{14}\text{N}_2 \cdot 2\text{HBr}$ and $\text{ZnI}_2 \cdot \text{C}_{10}\text{H}_{14}\text{N}_2 \cdot 2\text{HI}$.

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A STUDY OF CHITIN

I. ACTION OF ACIDS AND OF ALKALIES UPON CHITIN

S. N. Danilov and E. A. Plisko

It has been determined by chemical [1-4] and by physical [5, 6] investigations that chitin consists of monoacetylglucosamine residues joined by 1,4- β -glucosidyl bonds, with 180° rotation. Thus, the chitin macromolecule is constructed analogously to that of cellulose, but differs from the latter in that hydroxyl groups at the C₂ atoms are substituted by aminoacetyl groups, which apparently accounts for the differing properties of cellulose and chitin. As with cellulose, chitin is insoluble in water and organic solvent; in contrast to cellulose, it does not dissolve in ammoniacal copper solution, and swells but very little with rise in temperature.

Treatment of chitin with sodium hydroxide or potassium hydroxide at high temperature (up to 180°) leads to deacetylation and destruction of chitin, the so-called chitosan which results in possessing different properties from that of chitin (Gilson [7], Hoppe-Seyler [8]).

Chitosan prepared in such a manner [9] is obtained as a yellow, amorphous mass, insoluble in water and alkalies; readily soluble in dilute hydrochloric acid and acetic acid, and precipitated from these solutions by alkalies. Chitosan is found to be one of the products of extensive disintegration, and possibly oxidation, of chitin, data for which have been obtained by various authors [10, 11].

The present authors have used low temperature in order to avoid possible oxidation in the splitting of chitin in experiments concerning the relationship of chitin to alkalies.

It is known that the swelling of polysaccharides is an exothermic process; according to LeChatelier's principle, lowering of the temperature should favor an increase in swelling, which is confirmed by experiments (negative temperature coefficient of swelling).

Nikitin and coworkers have developed a method for freezing cellulose in alkalies and low molecular weight xanthogenates in 8% sodium hydroxide [12]. Taking into account the analogy in structure for chitin and cellulose, it can be postulated that decrease of temperature will result in an increased swelling in alkaline solutions, which has also been indicated by preliminary experiments described in the literature [13].

The authors have established that on cooling of alkaline solution down to freezing, with subsequent thawing, there is observed not just swelling of chitin upon its dissolution. Chitin samples separated after treatment of alkalies of various concentration, and at lowered temperature, have even swelled without limit (dissolved) in dilute organic and mineral acids. Analysis of the isolated samples for acetyl content has indicated that their content is considerably decreased because of hydrolysis under the conditions of alkali treatment. Preparations obtained by the authors, however, are still closely related to chitin and differ from chitosan described in the literature. More complete swelling of chitin in alkalies might be attributed to removal of acetyl groups, but chitin samples separated after treatment with alkalies did not swell at room temperature. Swelling at low temperature is apparently conditioned not by splitting off of acetyl groups, but by loosening the chitin strand structure.

Because of the fact that in treatment of chitin by alkali at low temperature there occurs considerable hydrolysis of acetyl groups, there then appear primary amino groups whose percentage content has been determined by the Van Slyke method [14]. The authors, however, did not succeed in completely removing acetyl groups to obtain the corresponding aminopolysaccharide.

The relationship of chitin to acids has received but little illumination in the literature.

Sulfuric (70-79%) [2] and hydrochloric [1, 3] acids have been used primarily for elucidation of the chitin structure.

It is known from the works of Eckenstamm [15] that the rate constant for cellulose hydrolysis in strong phosphoric acid is 200-fold less than in strong sulfuric acid; the authors therefore proposed to use phosphoric acid as the solvent in molecular weight determination by the viscometric method, and for fractionating cellulose. The authors have carried out experiments on dissolution of chitin in phosphoric acid, and the properties of the solutions and of chitin regenerated from solution have been studied.

Meyer and Wehrli have indicated [11] that phosphoric acid dissolves chitin at concentrations from 45 to 85% within an hour.

A thorough study of the authors' chitin samples with respect to solubility in phosphoric acid established that 40, 50 and 60% phosphoric acid does not dissolve chitin, even upon prolonged reaction time (up to 6 days). Partial dissolution was observed at concentrations from 70.10 to 76.73%, and complete dissolution took place at acid concentrations from 78.4 to 97.2% (Fig. 1). The authors have determined characteristic viscosities of chitin in phosphoric acid.

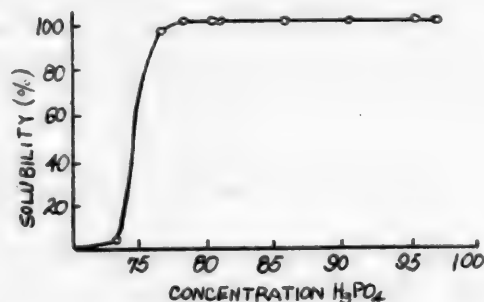


Fig. 1. Solubility of chitin in phosphoric acid

TABLE 1

Chemical composition of crab and crayfish chitin

Crude material	Sample number	Content found minus ash (in %)				Ash (in %)	Crude material	Sample number	Content found minus ash (in %)				Ash (in %)
		C	H	N	CH ₃ CO								
Crab chitin	1	46.96	6.65	6.68	20.02	0.23	Crayfish chitin	1	46.91	6.65	6.58	20.05	0.23
	2	46.72	6.67	6.70	20.30	0.14		3	46.76	6.82	6.24	19.94	0.33
	3	46.66	6.75	6.52	20.06	0.32		5	46.83	6.37	—	20.28	0.24
	4	46.95	6.77	6.48	19.80	0.14		6	46.92	6.70	6.65	20.28	0.22
	5	46.55	6.75	6.73	19.85	0.66							
	6	46.72	6.69	6.51	19.85	0.09							

Note: Theoretical content for $(C_8H_{13}O_5N)_n$ in % C 47.27; H 6.40; N 6.89; CH₃CO 21.13.

EXPERIMENTAL

Chitin for the experiments was obtained by the authors from crab shells (Far East) and from local crayfish [16-19]. The shells were cleaned of muscle remains and then ground in a rotary mill. The ground shell was then sifted through a set of sieves; shell of varying degrees of pulverization were thus obtained. The resulting shell was treated first with water and then with 5% hydrochloric acid. Following this, disintegration of protein and pigment substances was carried out by boiling the shell in a 5% solution of sodium hydroxide for 4 hours. The isolated chitin was washed repeatedly with water and dried at 105°. The pigment residue was removed by extracting with alcohol and benzene (1:1) mixture in a Soxhlet apparatus. The isolated chitin samples were of the chemical compositions given in Table 1.

Action of Alkalies upon Chitin

Chitin samples, obtained according to the above described procedure, were treated with alkali solutions of various concentrations at various temperatures. Experiments at -10, -20, -30 and -40° were carried out in a freezer with automatic temperature regulator and at -70° in a Dewar flask with solid carbon dioxide. It can be seen from

TABLE 2

Experiments on Treatment of Chitin at Various Alkali Concentrations at Low Temperatures

Sample No.	Experimental conditions	Properties of Chitin Samples after treatment with alkali
	Chitin treated with 4% NaOH	
1	At -10°; 8 hours, ratio 1:10	Samples 1-3 did not swell in concentrated or dilute organic acids. They dissolved in 60% H ₂ SO ₄ , 50.70% HNO ₃ , 37% HCl, 78.4 and 97% H ₃ PO ₄ . Sample 4 swelled a little in dilute acetic and formic acids. Soluble in concentrated mineral acids.
2	At -20°; 10 freezings, ratio 1:15	
3	At -30°; 14 freezings, ratio 1:15	
4	At -40°; 14 freezings, ratio 1:15	
	Chitin treated with 8% NaOH	
5	At -10°; 8 hours, ratio 1:10	Samples 5-7 had the same properties as samples 1-3. Samples 8, 9 and 13 swelled a great deal in dilute organic and mineral acids. Samples 10-12 dissolved in dilute 2-10% organic and mineral acids.
6	At -10°; 8 hours, ratio 1:10	
7	At -20°; 10 freezings, ratio 1:15	
8-9	At -30°; 14 freezings, ratio 1:15	
10-12	At -40°; 14 freezings, ratio 1:25	
	Chitin treated with 10% NaOH	
13	At -30°; 14 freezings, ratio 1:15	Samples 14 and 15 dissolved in dilute organic acids.
14-15	At -40°; 14 freezings, ratio 1:15	
	Chitin treated with 19.5% NaOH	
16	At -40°; 14 freezings, ratio 1:15	Samples 16, 17 swelled greatly and dissolved partially in dilute organic and mineral acids. Soluble in concentrated mineral acids.
17	At -70°; 14 freezings, ratio 1:15	
	Chitin treated with 30% NaOH	
18	At -30°; 14 freezings, ratio 1:15	Samples 18-20 swelled greatly in dilute organic acids; soluble in concentrated mineral acids.
19	At -40°; 14 freezings, ratio 1:15	
20	At -70°; 14 freezings, ratio 1:15	

TABLE 3

Amino Nitrogen in Samples After Treatment with Alkalies

Expt. No. and sample	4	8	10	11	12	13	14	15	16	17	18	19
Amino nitrogen (in %)	1.30	2.42	6.82	7.17	7.05	3.68	6.80	7.05	6.00	4.10	4.75	6.20

preliminary experiments that chitin swells but very little when treated with dilute sodium hydroxide solutions at -10 and -20° temperatures, since the chitin which separated after these treatments did not differ from the properties of the initial chitin (Table 2). By using a lower temperature, it was possible to put the chitin into solution (samples 10, 11, 12).

Thus in experiment No. 10, 125 ml of 8% sodium hydroxide solution was added to 5 g of chitin sifted through a 1 mm sieve. The flask was sealed with a cork and placed in the freezer, where -40° temperature was maintained, and after a given time interval freezing (20 minutes) was alternated with thawing at room temperature (1 hour). After 14 consecutive freezing and thawing operations, the authors succeeded in putting the chitin into solution. The solution was filtered through cheese cloth. If the solution was left at room temperature, then after a time lapse irreversible processes took place. After 2-4 weeks (depending upon the concentration of the solution), coagulation (precipitation) occurred, with gel formation, which did not break upon shaking. Upon storing the gel at room temperature, separation into two phases occurred — syneresis phenomenon.

The chitin solution obtained by alkali freezing, after filtering, was poured into a large volume of distilled water, whereupon chitin precipitated in highly dispersed form as large flakes. Washing was carried out with water and decantation. After removal of alkalies the chitin was separated on a filter, washed with methyl alcohol, acetone and ether. Drying was carried out in a vacuum desiccator without heating. Yield was 4.32 g (85.4% of chitin taken).

The preparation which separated, gray in color, was readily ground to a powder in a porcelain mortar, and dissolved in 2.25% acetic, 3% oxalic, dilute hydrochloric and sulfuric acids; swelled considerably in glacial acetic, formic and levulinic acids. It is necessary to note that this preparation did not swell after drying and did not dissolve in dilute alkalies at room temperature.

Experiments on freezing and thawing of alkalies with chitin are given in Table 2.

Analysis for acetyl content in the samples (as described by Brach) [16], indicated considerable decrease. Amino groups appearing instead were determined according to Van Slyke (Table 3).

From the data of Table 3, it can be seen that the amino nitrogen content in samples 4, 8, 13, 17 and 18 is negligible, while sample 18 content of amino nitrogen is higher than in other samples. This difference becomes understandable if one calculates the various alkali concentrations used in freezing. Moreover, it can be seen from the data of Table 3 that treatment of chitin with alkalies of various concentrations at -40° gave for the maximum amino nitrogen content for samples which dissolved or swelled greatly, with a sodium hydroxide concentration of 8 and 10 %.

For samples 10 and 14 in 2.26% aqueous acetic acid, from viscosity-concentration curves, $\frac{\eta_{sp}}{c}$ versus c (in g/100 ml), were found: $[\eta]$ 34.0 for sample 10 and $[\eta]$ 30.0 for sample 14, which considerably exceeded the characteristic viscosity values for chitin in 80.4% phosphoric acid. It is possible that deacetylated chitin is more readily soluble than chitin itself in organic and mineral acids, forming salts characterized by high viscosities.

For purposes of the reverse process of introducing acetyl groups into partially deacetylated chitin, acetylation of samples 10 and 16 with acetyl chloride was carried out in chloroform medium at room temperature for 14 days, and also with acetyl chloride for 3 hours, heating the acetyl chloride to boiling. With such treatment, however, there was no acetylation of the samples; the authors therefore used the procedure of acetylation with acetic anhydride in a sealed tube at 100° for 4 hours. As acetylation proceeded, a change in color of the initial samples was observed (from gray to a light yellow) as well as an increase in volume of the substance.

For sample 10 after acetylation there was found, according to analysis, the following (average of two determinations) in %: C 46.69; H 5.41; N 5.17; CH_3CO 20.20, which differed somewhat from analysis of the initial crab chitin (Table 1) in favor of oxygen enrichment and lowering of hydrogen and nitrogen contents; non-coincidence of numbers may be due to some hydrolysis of amino groups while treating with alkalies, which was not directly confirmed, however. Analysis for nitrogen was carried out according to Dumas and Kjeldahl.

Acetylated samples did not dissolve in, nor swell in, dilute organic acids; soluble in concentrated hydrochloric, 78-95% phosphoric, 60% sulfuric, 50.7% nitric acids, while dissolution was slower than for the initial chitin. Thus, with dissolution of chitin in 50.7% nitric acid, there was observed immediately after mixing a marked swelling and dissolution, whereas the samples treated with alkali in the cold and reacetylated, dissolved after a lapse of 18-20 hours. Apparently in the case given, greater or less density plays a role in gradual loosening of the substance.

The initial chitin had high porosity, while samples treated with alkali and then acetylated were in the form of a horny mass, and consequently solvent penetration was slower.

On the basis of experiments on chitin freezing in alkalis at various temperatures, it can be deduced that the maximum swelling of chitin proceeds at 8-10% sodium hydroxide and a temperature of -40° . Under such conditions dissolution of chitin in sodium hydroxide also proceeded in sodium hydroxide of the indicated concentrations. Moreover, hydrolytic rupture of the chitin acetyl groups proceeded, and partially deacetylated chitin resulted.

Relation of Chitin to Phosphoric Acid

Determination of solubility of chitin in phosphoric acid was carried out at room temperature.

An weighed sample of absolutely dry chitin was stirred with the same amount of phosphoric acid in order to obtain a solution of concentration of 0.5 g in 100 ml. The acid was added dropwise from a buret. After addition of all acid, stirring was carried on periodically for 10-15 minutes. After 5 hours the suspension was filtered through a porous plate, and the residue washed on the filter with the same acid, then with water to a neutral reaction, and dried on the filter to constant weight at 105° .

The solubility was calculated in percentage of the content of absolutely dry chitin relative to initial batch. If the batch dissolved completely, which could be judged by a sample in the polarizing microscope, then the solution was not filtered and the solubility was marked as 100% (Fig. 1).

Because of the fact that obtaining a concentrated solution of chitin in phosphoric acid is possible only under conditions of prolonged reaction, which may cause hydrolysis, the authors investigated the effect of time upon the properties of the solution in phosphoric acid and regenerated chitin (Table 4).

TABLE 4

Properties of chitin separated from solution immediately after storing. (80.4% acid, 4% chitin solution, temperature 17°)

Expt. No.	Dissolution time (in hours)	Additional heating	Copper number		Content of acetyl (in %)	
			Chitin		Chitin	
			of crayfish	of crab	of crayfish	of crab
1	5	—	1.22	2.84	20.16	20.00
2	5	1 hour at 40°	2.52	4.37	20.25	—
3	5	1 hour at 50°	6.10	7.65	—	20.10
4	24	—	4.34	4.57	—	—
5	48	—	5.68	5.52	—	—
6	72	—	7.20	7.50	20.15	20.00
7	96	—	8.75	8.54	—	—

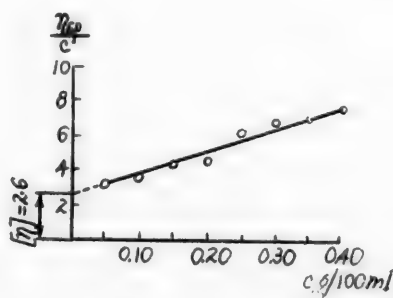


Fig. 2. Concentration curve for viscosity of chitin solution from crabs in 80.4% H_3PO_4 .

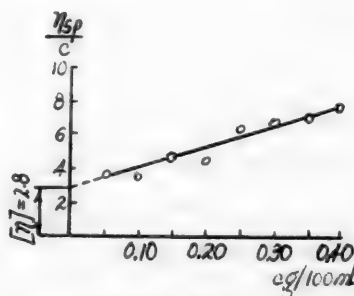


Fig. 3. Concentration curve of viscosity for crayfish chitin solutions in 80.4% H_3PO_4 .

From concentrated solutions of chitin in phosphoric acid there can be prepared films 18-20 hours after dissolution, while at the same time films can be made from concentrated chitin solution in nitric acid 1 hour after

dissolution. From the indicated concentrated solutions of chitin, the authors obtained layers which were intensely colored by wool dyes.

Dependence of solution viscosity on concentration for chitin of crayfish and of crab in 80.4% phosphoric acid was determined.

To determine this relationship, specific solutions were prepared of specific concentration by the weight method. The viscosity was determined in an Ostwald viscometer, 10 ml in volume. The viscometer was placed in a thermostat, where a constant temperature of $20^{\circ} \pm 0.01^{\circ}$ was maintained.

On the basis of data experimentally obtained by the authors, curves were constructed for concentration ratio $\frac{\eta_{sp}}{c} = f(c)$, extrapolation of which to zero concentration (Figs. 2,3) gave values for the intrinsic viscosity [2]. Thus it can be seen that the characteristic viscosities of crayfish and crab chitin are approximately the same, which may indicate the same length of macromolecule for crayfish and for crab chitin.

SUMMARY

1. It has been demonstrated that with repeated freezing of chitin in alkali and with subsequent thawing at room temperature, swelling proceeds, and even dissolution. Maximum swelling and dissolution results at 4% chitin concentration and 8 and 10% NaOH at a temperature of -40° .

2. Upon repeated freezing of chitin with subsequent thawing, there occurs a partial hydrolysis of acetyl groups, and their maximum hydrolysis corresponds to an NaOH concentration of 8 and 10%, and a temperature of -40° , i. e., maximum hydrolysis proceeds under the same conditions which produce considerable swelling and dissolution of chitin.

3. It has been established that 40, 45, 50 and 60% H_3PO_4 does not dissolve chitin, even upon prolonged reaction time, which contradicts literature data relative to the solubility of chitin in 45% phosphoric acid.

4. Complete dissolution of chitin proceeds at phosphoric acid concentrations in the range 78.40-97.20%. Higher concentrations of the acid are not convenient, since, on addition of chitin, there takes place crystallization of acid, and chitin does not swell.

Hydrolysis of chitin occurs over a period of time, as can be seen from increase in copper number of the samples.

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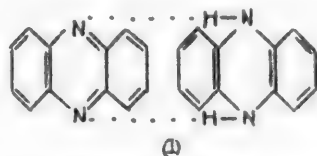


STUDY OF THE MOBILITY OF HYDROGEN ATOMS IN

PHENAZOHYDRIN HYDROGEN BONDS

I. P. Gragerov

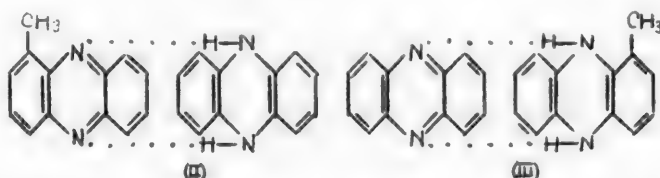
The phenazohydrins closely resemble the quinhydrone. The structure of these substances has not been clearly elucidated. The literature contains several variations for their structure [1], of which (I) seems probable, with the component molecules held by hydrogen bonds and situated in parallel planes.



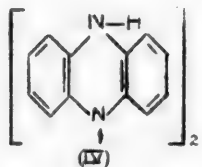
In our earlier work [2] in which benzoquinhydrone was studied by the isotope method, it was shown that the hydrogen in the hydrogen bonds in this substance is localized at the hydroquinone nucleus and can only be displaced to the other nucleus on heating with an activation energy of about 32 kcal/mol.

In the present study the isotope method was used for the solution of analogous problems of phenazohydrin structure, and for this purpose, as in the work with quinhydrone, phenazohydrin was prepared from heavy phenazine and ordinary dihydrophenazine and then separated into its components. Although the conditions for the preparation and separation of this substance were close to those used in the work with quinhydrone, the opposite result was obtained: the deuterium was equally divided between the phenazine and the dihydrophenazine, which appears to indicate that the nuclei of these substances in the phenazohydrin molecule are equivalent.

Analogous results were previously obtained by Clemo and McIlwain [1]. They showed that the phenazohydrins, which should have the structures (II) and (III) according to their method of preparation, are identical.



However, our results and those of Clemo and McIlwain cannot be considered as proof of the equivalence of the component nuclei in phenazohydrin, as they have another explanation, and furthermore both the possible variants of structure with equivalent nuclei are unsatisfactory. The Structure (IV) does not explain the very easy dissociation of phenazohydrin into its components in solution. Structure (I) with a delocalized hydrogen bond hydrogen is improbable, as phenazohydrin should be analogous to benzoquinhydrone with regard to hydrogen mobility in the hydrogen bonds. Indeed, in its molecule hydrogen can be displaced only as a neutral atom and with the same bond rearrangement as in benzoquinhydrone. As regards the mobility of the hydrogen, the great N-N distance and the low energy of the hydrogen bond with nitrogen, with a high value for the energy of the N-H bond, suggest that the potential barrier for hydrogen displacement in phenazohydrin is high, and is not lower than in benzoquinhydrone. On the basis of these considerations and the chemical behavior we believe that phenazohydrin has Structure (I), with the hydrogen atoms localized at the dihydrophenazine nucleus.



The most natural explanation of the results of this work is that during preparation of phenazohydrin an oxidation-reduction equilibrium is set up in the solution between the doubly charged negative dihydrophenazine ion and

phenazine, similarly to the well-known effect in quinhydrones. Another possible explanation presupposes the formation in the solution of small concentrations of radicals of the same type (IV in monomer form) from both components, leading to equal distribution of deuterium between the nuclei. Clemo and McIlwain's results are explained similarly.

Heavy phenazine* was prepared by heating phenazine with D₂O in the presence of a small amount of sulfuric acid for 48 hours at 185°. No exchange takes place in the same conditions but in the presence of alkali.

Heavy phenazohydrin was prepared by two methods: by evaporation of an ether solution of equimolar amounts of the components in a stream of CO₂, or by mixing saturated dioxane solutions of the components at room temperature.

The resolution into the components was effected in two ways. a) 0.09 g of heavy phenazohydrin was heated to 96° at 10⁻⁴ mm in the previously described quartz apparatus 20 mm in diameter, when the phenazine sublimed on the cold walls while the dihydrophenazine remained in the lower part of the apparatus. The resolution was completed in 1.5 hours. The melting point of the phenazine was 174-174.5°, and that of the dihydrophenazine 210.7°. The yield was almost quantitative. b) An ether solution of equimolar amounts of heavy phenazine and dihydrophenazine was passed in a stream of nitrogen through an aluminum oxide column, followed by washing with ether, when first phenazine and then a mixture of phenazohydrin and dihydrophenazine entered the receiver.

Isotope analysis. The phenazine and dihydrophenazine, or phenazine and the mixture of phenazohydrin and dihydrophenazine (in the chromatographic separation experiments) were burnt, and the water after the combustion was analyzed for deuterium content by the microflotation method with an accuracy of $\pm 3\%$.

It was found that, regardless of the method used for the preparation and separation of the phenazohydrin, the deuterium contents of its components were the same within the limits of experimental error: they were from 47 to 49% of the original amount of deuterium in the phenazine, and from 48 to 49.5% in the dihydrophenazine.

During the development of the chromatographic separation method it was found that heavy benzoquinhydrone can also be separated by this method; the quinone and quinhydrone obtained contain equal amounts of deuterium. A control experiment showed that when an ether solution of quinhydrone was kept 5 hours at room temperature, followed by separation by means of vacuum distillation, the deuterium contents in the quinone and hydroquinone were not equal. The catalytic effect of aluminum oxide on the transfer of hydrogen in quinhydrone is analogous to the effect of glass which was previously observed by us.

SUMMARY

1. It was found that phenazohydrin prepared from heavy phenazine and ordinary dihydrophenazine yields phenazine and dihydrophenazine with equal deuterium contents when resolved into its components.
2. This is explained by the fact that when phenazohydrin is prepared, an oxidation-reduction equilibrium is set up in solution between the negative doubly charged dihydrophenazine ion and phenazine.
3. Structure (I), with localized hydrogen bond hydrogen, is adopted for phenazohydrin.

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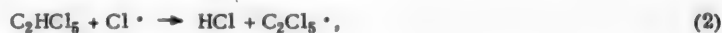
* The experiments were performed with the assistance of T. G. Lando and Yu. Ya. Fialkov.

** T. p. = C. B. Translation pagination.

PHOTOLYSIS OF PENTACHLOROETHANE

G. A. Razuvaev and N. A. Osanova

In an investigation of photochemical reactions in solutions of polyhalogenated compounds we observed the decomposition of pentachloroethane which proceeds with evolution of hydrogen chloride. It was first presumed that the formation of perchloroethylene according to the following Scheme is possible in this reaction:

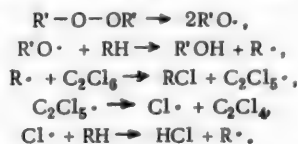


In reality the process is much more complicated, as we were able to obtain from the reaction products a number of chlorine derivatives of butane, namely: heptachlorobutane, octachlorobutane, nonachlorobutane, decachlorobutane, and also hexachloroethane. A more detailed investigation of this reaction was therefore of interest. By analogy with the thoroughly studied reactions of the decomposition of carbon tetrachloride [1], the photolysis of pentachloroethane is undoubtedly a radical mechanism reaction which proceeds with the removal of chlorine and the formation of the tetrachloroethyl radical (1). From this, chlorinated butanes may be obtained either by dimerization of the radicals formed, or by the addition of polyhalogenated ethane derivatives to unsaturated compounds [1]. The formation of unsaturated compounds is possible as the result of the decomposition of chlorinated ethyl radicals (3), which is confirmed by a number of studies. For example, in the thermal decomposition of hexachloroethane chlorine is split off and the pentachloroethyl radical is formed:

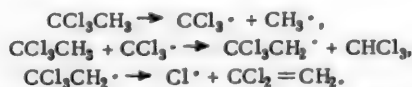


which then decomposes to form perchloroethylene.

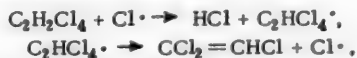
Perchloroethylene is formed in free radical reactions of saturated hydrocarbon chlorination [2], initiated by tertiary butyryl- or benzoyl peroxides, according to the Scheme:



The literature also contains indications of the decomposition of other chlorinated ethyl radicals. For example, in the pyrolysis of 1,1,1-trichloroethane [3], the trichloroethyl radical formed decomposes with the formation of vinylidene chloride:



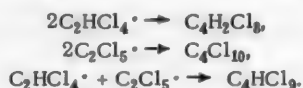
The thermal decomposition of tetrachloroethanes proceeds with the formation of trichloroethylene [4] owing to decomposition of the tetrachloroethyl radical:



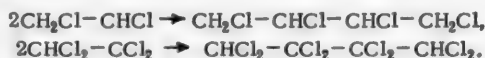
It is possible that the unsaturated compounds formed in the photolysis of pentachloroethane can add on to the latter to form chlorinated butane derivatives



On the other hand, as was already pointed out, the chlorinated ethyl radicals (1) and (2) may dimerize to form octachlorobutane, decachlorobutane, and also nonachlorobutane:



The literature contains numerous references [1] to the possible dimerization of the CCl_3 radical and also of the CH_2Cl radical obtained in the decomposition of CH_3Cl photosensitized by mercury [5]. The dimerization of radicals of the ethane series has also been reported. For example, dichloroethyl and tetrachloroethyl radicals are dimerized to form tetrachlorobutane and octachlorobutane in the thermal reaction of benzoyl peroxide with 1,2-dichloroethane and 1,1,2,2-tetrachloroethane [6]:

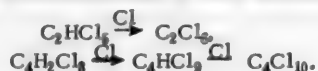


Numerous instances of radical dimerization have also been observed in the thermal reaction of acetyl peroxide with various types of substituted hydrocarbons of the methane and ethane series [7]. In the photolysis of pentachloroethane radical dimerization is more probable, as the decomposition of chlorinated ethane radicals usually occurs at higher temperatures. From the reaction products it may be supposed that two processes occur in the reaction:

1) dimerization of the tetrachloroethyl radicals initially formed according to Equation (1), with the formation of octachlorobutane:



2) the chlorination, by the chlorine formed, both of the original pentachloroethane to form hexachloroethane, and of the dimerization product of octachlorobutane to form nonachlorobutane and decachlorobutane



The formation of decachlorobutane could also be attributed to dimerization of pentachloroethyl radicals, but more probably it is formed according to the above chlorination reaction. The latter is also confirmed by the following: in experiments with comparatively short irradiation times the amount of octachlorobutane was relatively greater, while upon prolonged irradiation the amount of octachlorobutane decreased and that of nonachlorobutane and decachlorobutane increased. The formation of heptachlorobutene could be explained by the removal of the elements of hydrogen chloride from octachlorobutane during vacuum distillation of the reaction mixture.

The formation of tarry matter indicates that the photolysis of pentachloroethane is also accompanied by a number of other side reactions.

EXPERIMENTAL

Synthesis of pentachloroethane. Pentachloroethane was prepared by chlorination of trichloroethylene under irradiation. The reaction product was washed with weak solutions of soda, sulfite, and water; it was dried over calcium chloride and fractionated. The fraction with b.p. 159-162° and n_D^{20} 1.5030 was collected. Literature data: b. p. 162° n_D^{20} 1.5054 [9].

Photolysis of pentachloroethane. Pentachloroethane was irradiated in quartz test tubes, 20 mm diameter, by ultraviolet light from a PRK-2 lamp for a long time (from 250 to 500 hours) at a distance of 200 mm from the lamp. The irradiation was accompanied by evolution of hydrogen chloride, which was absorbed by solid alkali contained in traps specially attached to the stoppers of the tubes. It was necessary to change the alkali from time to time. The combined photolysis product from several tubes was washed with weak soda solution to remove hydrogen chloride and then with water, dried over calcium chloride, and distilled in vacuum: the unreacted pentachloroethane distilled at 65-75° and 75-80 mm. The last pentachloroethane fractions contained hexachloroethane, which was obtained pure by a repeated distillation of the pentachloroethane over a large plate-type distillation column. The oily liquid which remained after removal of the pentachloroethane was distilled under vacuum. The evolution of hydrogen chloride and formation of tarry matter was observed in the process. Preliminary analysis of the distilled liquid showed that it was a mixture of chlorinated derivatives of the butane series. The mixture obtained in a large number of experiments was repeatedly fractionated under vacuum in order to separate it into its components. The following were isolated in the separation:

1) Heptachlorobutene, b.p. 110-120° at 5 mm, n_D^{20} 1.5529. Literature data [8]: b.p. 210° at 760 mm, n_D^{20} 1.5529.

Found %: Cl 83.59, 83.14, 83.38; M 286.59, 287.65, 285.37. C_4HCl_7 . Calculated %: Cl 83.50; M 297.3.

The reaction of heptachlorobutene with alcoholic alkali yielded hexachlorobutadiene: 2.23 g of the substance was dissolved in ethyl alcohol, the solution was cooled, and a cooled 0.1 N alcoholic KOH solution was added with phenolphthalein indicator. The product after removal of the hydrogen chloride was precipitated by water, dried over calcium chloride, and distilled under vacuum. The yield was 0.6 g of a substance with b.p. 210° at 760 mm (by Sivolobov's micro method) n_D^{20} 1.5532. Literature data [8,9]: b.p. 210° at 760 mm, n_D^{20} 1.5531.

Found %: Cl 82.04, 82.19; M 260.73. C_4Cl_6 . Calculated %: Cl 81.58; M 260.8.

2) Octachlorobutane, white rhombic crystals, m.p. 78° (from ethyl alcohol). Literature data [10]: m.p. 75-76°.

Found %: Cl 85.01, 84.80, 84.50; M 318.63, 315.38, 319.62. $C_4H_2Cl_8$. Calculated %: Cl 85.03; M 333.7.

3) Nonachlorobutane, b.p. 150-160° at 5 mm, n_D^{20} 1.5798. Literature data [8]: n_D^{20} 1.5798, b.p. 123° at 0.1 mm.

Found %: C 13.20, 12.93; H 0.31, 0.30; Cl 86.45, 86.28; M 354.26, 362.49, 360.0. C_4HCl_9 . Calculated %: C 13.05; H 0.27; Cl 86.68; M 368.2.

The action of alcoholic alkali on nonachlorobutane yielded octachlorobutene. 12.14 g of the substance was treated with alcoholic KOH solution as previously. 5 g of a substance with b.p. 125-130° at 6 mm, and n_D^{20} 1.5784, was distilled under vacuum. Literature data [8]: b.p. 97° at 0.1 mm, n_D^{20} 1.5789.

Found %: Cl 84.91, 85.17; M 319.75, 317.62, 324.48. C_4Cl_8 . Calculated %: Cl 85.53; M 331.7.

4) Decachlorobutane, white crystals, had m.p. 98° after repeated recrystallization from methyl alcohol. Literature data [8]: m.p. 101°.

Found %: Cl 88.05, 88.00, 88.13; M 383.13, 390.34, 382.61. C_4Cl_{10} . Calculated %: Cl 88.07; M 402.6.

5) Hexachloroethane, m.p. 185° sublimed over concentrated H_2SO_4 and gave no melting point depression with the pure substance. Literature data: m.p. 186.9 ~ 187.4° [11].

In the course of a series of experiments it was observed that the amount of decachlorobutane formed increased, and that of octachlorobutane decreased, with increase irradiation time. In some instances octachlorobutane was not isolated in solid form after prolonged exposure. As an example we give the results of one of the experiments carried out with prolonged irradiation (500 hours). The 500 g of pentachloroethane taken, after removal of the unreacted compound, yielded 17 g of hexachloroethane and 50.5 g of an oily product, from which 39 g of a mixture of polyhalogenated butane derivatives and 9 g of resin was obtained by distillation. The following fractions were obtained by vacuum distillation of the polyhalogenated mixture: first, b.p. 100-125° at 5 mm, 6.5 g, which was heptachlorobutene; second, b.p. 127-145° at 5 mm, 5.5 g, a mixture of 70% heptachlorobutene and 30% octachlorobutane, as confirmed by analyses of this fraction and conversion of it into hexachlorobutadiene by the action of alcoholic alkali.

Found %: Cl 84.01, 83.87, 83.79; M 323.48, 325.09, 322.86. Calculated octachlorobutane content: 28.75.

4.26 g of substance after treatment with alcoholic alkali: 2.5584 g $AgCl$. Calculated octachlorobutane content: 31.39%.

The third fraction, b.p. 148-160° at 5 mm, 24.4 g, was a mixture of 66.6% nonachlorobutane and 33.4% decachlorobutane. To isolate the latter, the fraction was treated with alcoholic alkali. This converted nonachlorobutane into octachlorobutene, which was distilled off to leave 8.17 g solid decachlorobutane. Thus, the nonachlorobutane content was 16.23 g. The residue after distillation of the polyhalogenated mixture (39 g) was 2.6 g of resin.

SUMMARY

1. It is shown that when pentachloroethane is irradiated by ultraviolet light hydrogen chloride is evolved and chlorinated butane derivatives are formed: octachlorobutane, nonachlorobutane, decachlorobutane, and also hexachloroethane.

2. A reaction scheme is proposed: the primary process is removal of a chlorine atom from pentachloroethane with the formation of tetrachloroethyl radicals, which dimerize to octachlorobutane. The chlorine evolved chlorinates both the original pentachloroethane, and the octachlorobutane formed, to yield nona- and decachlorobutane.

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FREE RADICAL REACTIONS IN SOLUTIONS

II. RELATIVE ACTIVITY OF FREE RADICALS IN REACTIONS WITH ISOPROPYLBENZENE, CYCLOHEXENE AND POLYMERS

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The activity of free radicals in their interaction with solvents (LH) is usually characterized by the extent to which the following reaction proceeds:



From the yield of the product RH it is at the same time possible to evaluate the mobility of the H atoms of the solvent reacting with the free radicals. This criterion was used in a number of investigations, including studies of the decomposition of metalorganic compounds in various media [1, 2], in the electrolysis of Grignard reagents [3], in studies of the photolysis products of aliphatic ketones [4], and in the pyrolysis of peroxides [5]. A strict generalization of the experimental data obtained in these studies is not possible because of the very diverse experimental conditions used. In the present study data on the relative activities of a number of free radicals, which differ considerably from each other in reactivity, were obtained on the basis of a study of the thermal decomposition products of diazoamino compounds in solution. The decomposition, which proceeded according to the Equation



took place under temperature conditions which ensured comparable decomposition rates of the diazoamino compounds, which were used in molar concentrations of 1.2-1.3%. In addition to determination of the yields of the products RH, a full study of the final reaction mixtures was made for many of the original compounds, and the yields of products obtained by other reactions, in particular:



were determined.

The main results of the investigation are given in Tables 1 and 2, which also include data obtained in a study of the decomposition products of azoisobutyronitrile.

In addition to the compounds formed according to Reactions (1), (3), (4), and (5), the triazene decomposition products contain about 30% of aniline [or diphenylamine in the case of di(diphenyl) triazene].

Most probably only a small part of it is formed by the reaction



as there are no reasons for supposing that the activity of the anilino radical is so high. Indirect evidence of the low activity of the $C_6H_5NH \cdot$ radical is its inability to bring about vulcanization, as will be shown below. The fact that Reaction (6) nevertheless occurs is confirmed by the formation of the L-L product (dicumyl and dicyclohexenyl) in the decomposition of allyl- and benzylphenyltriazenes, that is, in cases when there is practically no removal of H atoms from isopropylbenzene by the free hydrocarbon radicals.

The free radical disproportionation reaction of the type



proceeds to a slight extent in the experimental condition used (Table 3).

The total absence of aliphatic amines in the alkyl aryl triazene decomposition products indicates that of the two possible structures

TABLE 1

Conversion Products of Free Radicals in Isopropylbenzene

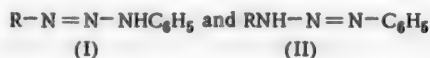
Original Compound		Temp. of Exp.	Yield (in %)			
Name	Formula		RH	R-R	R-NHAr	L-L
Methylphenyltriazene	$\text{CH}_3\text{N}=\text{N}-\text{NHC}_6\text{H}_5$	120°	56	0	26	17
Ethylphenyltriazene	$\text{C}_2\text{H}_5\text{N}=\text{N}-\text{NHC}_6\text{H}_5$	120	30	0	—	—
n-Propylphenyltriazene	$\text{C}_3\text{H}_7\text{N}=\text{N}-\text{NHC}_6\text{H}_5$	120	20	0	25	6
Isopropylphenyltriazene	$(\text{CH}_3)_2\text{CHN}=\text{N}-\text{NHC}_6\text{H}_5$	120	9	0	25	3
n-Butylphenyltriazene	$\text{C}_4\text{H}_9\text{N}=\text{N}-\text{NHC}_6\text{H}_5$	120	10	12	29	8
sec-Butylphenyltriazene	$\begin{array}{c} \text{CH}_3 \\ \\ \text{C}_2\text{H}_5-\text{CH}-\text{N}=\text{N}-\text{NHC}_6\text{H}_5 \end{array}$	120	6	—	—	—
tert-Butylphenyltriazene	$(\text{CH}_3)_3\text{CN}=\text{N}-\text{NHC}_6\text{H}_5$	110	0	0	30	—
Allylphenyltriazene	$\text{C}_3\text{H}_5\text{N}=\text{N}-\text{NHC}_6\text{H}_5$	120	0,2	13	34	3
Crotylphenyltriazene	$\text{C}_4\text{H}_7\text{N}=\text{N}-\text{NHC}_6\text{H}_5$	100	0	—	35	—
Benzylphenyltriazene	$\text{C}_6\text{H}_5\text{CH}_2\text{N}=\text{N}-\text{NHC}_6\text{H}_5$	120	0	25	29	3
di(Diphenyl)triazene	$\text{C}_6\text{H}_5\text{C}_6\text{H}_4\text{N}=\text{N}-\text{NHC}_6\text{H}_4\text{C}_6\text{H}_5$	140	46	5	—	9
Azoisobutyronitrile	$\begin{array}{c} (\text{CH}_3)_2\text{C}-\text{N}=\text{N}-\text{C}(\text{CH}_3)_2 \\ \quad \quad \\ \text{CN} \quad \quad \text{CN} \end{array}$	80	10	82	—	6

TABLE 2

Conversion Products of Free Radicals in Cyclohexene. (Decomposition Temperature 120°)

k [*]	Yield (in %)					
	RH	R-R	R-NHC ₆ H ₅	L-L [*]	L-R	L-NHC ₆ H ₅
$\text{CH}_3\cdot$	61	0	17	51	0	6
$\text{C}_6\text{H}_5\text{CH}_2\cdot$	0	20	34	24	6	0
$(\text{CH}_3)_2\text{C}-\text{CN}$	16	65	—	0	12	—
$\text{C}_2\text{H}_5\cdot$	45	Reaction mixtures not studied				
$n\text{-C}_3\text{H}_7\cdot$	29					
$n\text{-C}_4\text{H}_9\cdot$	5					
$\text{CH}_2=\text{CH}-\text{CH}_2\cdot$	2					

* The methylphenyltriazene decomposition products also contained tercyclohexenyl (L-L-L) in 6% yield.



only Structure (I) exists, at least at the time of decomposition.

It must be pointed out that Razuvaev, Fedotova, and Ovchinnikova, who studied the decomposition products of benzylphenyltriazene in carbon tetrachloride and ethylene glycol monoethyl ether [6], reached somewhat different conclusions on the decomposition mechanism of triazenes. It is possible that the specific peculiarities noted in the paper cited are due to the experimental conditions, which differed considerably from ours (in particular, the use of polar solvents and the presence of mercury).

From the results shown in Tables 1 and 2 it follows that Reaction (I) proceeds to a greater extent in the case of cyclohexene, which accounts for the increased yields and numbers of conversion products of the solvent radicals L^{*}. No products of the addition of free radicals to the cyclohexene double bonds were isolated in any instance. This indicates the much lower reactivity of internal double bonds in comparison with α -methylene groups, in agreement with literature data [7].

In the case of hydrazobenzene it was shown that when the reaction medium used is a compound with particularly mobile hydrogen atoms, the Reaction (I) may be brought about even for such free radicals as allyl and crotyl (Table 4).

TABLE 3
Extent of the Disproportionation Reaction of Alkyl Free Radicals
in Isopropylbenzene Solution*

C_nH_{2n+1}	Yield of C_nH_{2n} (in %)
$C_2H_5\cdot$	1
$n-C_3H_7\cdot$	1
$iso-C_3H_7\cdot$	3
$n-C_4H_9\cdot$	1
$sec-C_4H_9\cdot$	1
$tert-C_4H_9\cdot$	6

* The data on the yields of the products RH (Tables 1 and 2) are given with a correction by the subtraction of the amount of RH formed by Reaction 7.

TABLE 5
Yields of RH Products in Benzene Solutions of Rubbers at 120°

Radical	Yield of RH (in %)		
	in benzene	in natural rubber solution	in polybutadiene solution containing about 50% of 1, 2 links
$CH_3\cdot$	12	27	19
$C_2H_5\cdot$	8	18	10
$n-C_3H_7\cdot$	6	15	9
$n-C_4H_9\cdot$	0	5	5
$CH_2=CH-CH_2\cdot$	0	0.3	0.5

TABLE 4
Yields of RH Products of the Thermal Decomposition of Triazene in Hydrazobenzene at 131°

$R\cdot$	RH (in %)
$CH_3\cdot$	65
$CH_2=CH-CH_2\cdot$	8
$CH_3-CH=CH-CH_2\cdot$	6

In view of the fact that Reaction (1) is one of the causes of branching under polymerization conditions, it appeared of interest to determine the activity of free radicals in this reaction in relation to polymer molecules. For this purpose a study was made of the gaseous products formed in the decomposition of triazenes in benzene solutions of polyisoprene and polybutadiene (Table 5).

The formation of RH products during the decomposition of some triazenes in pure benzene is most likely caused by interaction between free radicals and triazene decomposition products, as, according to the literature [2], the possibility of Reaction (1) occurring in the case of benzene is doubtful.

The vulcanizing power of triazenes was chosen as another criterion of the relative activities of free radicals toward polymers, since the initial stages which lead to vulcanization are associated with reactions of the type



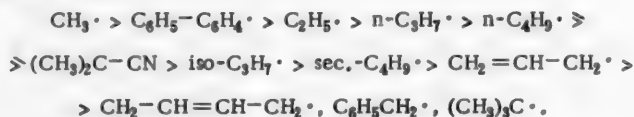
TABLE 6
Yield of Gel Fraction in the Bulk Vulcanization of Natural Rubber at 120° (Amount of Initiator was Equivalent to 5% by Weight of Benzoyl Peroxide)

Initiator	Heating time (min)	Yield of gel fraction (in %)	Initiator	Heating time (min)	Yield of gel fraction (in %)
Di(diphenyl)triazene	5	0	Isopropylbenzene hydroperoxide	40	8
	10	65		60	18
	20	76		120	28
	60	90		240	68
Diazoaminobenzene	5	0	Benzoyl peroxide	2	11
	10	21		5	60
	30	65			
	60	84			
Methylphenyltriazene	120	13	Allylphenyltriazene	300	0
	240	44	Benzylphenyltriazene	300	0
	360	48			

The vulcanizing action was measured by the degree of formation of the insoluble form (gel fraction) when natural rubber was heated with various sources of free radicals (Table 6). For comparison, this Table also contains data on the vulcanizing action of benzoyl peroxide and isopropylbenzene hydroperoxide.

The absence of gel fraction in the decomposition of allyl- and benzylphenyltriazenes in the bulk of the rubber also indicates the low activity of the anilino radical formed during the decomposition of triazenes (Reaction 2).

In accordance with the above results, the relative free radical activities in the hydrogen atom removal reaction may be expressed by the following series:



EXPERIMENTAL

Synthesis of triazenes. Methyl-, n-butyl-, allyl-, and benzylphenyltriazenes were prepared by the action of phenyldiazonium chloride on the corresponding amines [8]. Di(diphenyl)triene was synthesized by the passage of carbon dioxide through an alcohol solution of p-aminodiphenyl containing potassium chromate and sodium nitrite [9]. All the other triazenes were prepared by the action of the corresponding alkylmagnesium bromides on phenyl azide [10]. Only data on triazenes synthesized for the first time are given below.

Propylphenyltriene. Colorless crystals:

m.p. 16.5-18°, d_4^{20} 1.0125, n_D^{20} 1.5810.

Found %: C 66.05, 65.70; H 8.06, 7.93; N 25.82, 26.10. M 162, 165. $\text{C}_9\text{H}_{13}\text{N}_3$. Calculated %: C 66.25; H 7.97; N 25.76. M 163.

Isopropylphenyltriene. Pale yellow oil:

d_4^{20} 1.0073, n_D^{20} 1.5750.

Found %: C 65.90, 65.50; H 7.93, 7.87; N 25.86, 25.88. M 162.5, 162. $\text{C}_9\text{H}_{13}\text{N}_3$. Calculated %: C 66.25; H 7.97; N 25.76. M 163.

n-Butylphenyltriene. Colorless crystals:

m.p. 17-18°, d_4^{20} 0.9921, n_D^{20} 1.5690.

Found %: N 23.40, 23.00. M 174, 178. $\text{C}_{10}\text{H}_{15}\text{N}_3$. Calculated %: N 23.67. M 177.

The silver derivative forms bright yellow crystals, m.p. 101-102°.

sec-Butylphenyltriene. This was not isolated pure. The crude product was a dark oil which contained, according to the amount of nitrogen evolved on pyrolysis, 54% of the triene.

tert-Butylphenyltriene. Dark brown oil. The silver derivative forms pale yellow crystals, m.p. 149°.

Found %: Ag. 37.65. $\text{C}_{10}\text{H}_{14}\text{N}_3\text{Ag}$. Calculated %: Ag 38.00.

Allylphenyltriene. Colorless crystals:

m.p. 8-10°, d_4^{20} 1.0070, n_D^{20} 1.5551.

Found %: N 25.75, 25.69. M 164, 164. $\text{C}_9\text{H}_{11}\text{N}_3$. Calculated %: N 26.04. M 161.

The silver derivative forms pale yellow crystals, m.p. 132° (decomp.).

Crotylphenyltriene. This was not isolated pure. The crude product was a dark oil which contained, according to the amount of nitrogen evolved on pyrolysis, 80% of the triene.

Di(diphenyl)triene. Pale yellow needles: m.p. 147.5-148°.

Found %: N 12.22, 11.70. M 343, 340. $\text{C}_{24}\text{H}_{19}\text{N}_3$. Calculated %: N 12.02, M 349.

Investigation of the decomposition products. The original compounds were decomposed in ampoules connected to gas burets by long necks. The ampoule necks were provided with cooling jackets. In the cases of cyclohexene and benzene the decomposition was carried out under 750-800 mm excess pressure, which was regulated by means of an open mercury manometer connected to the system. The decomposition was continued till gas evolution ceased, which usually required 5-6 hours. The gaseous products were analyzed with the aid of the VTI gas analyzer. A metal cap

column was used for the distillation of the reaction mixture. The residue after removal of the main bulk of solvent was treated with hydrochloric acid to separate the amines. The primary and secondary amines were separated with the aid of metaphosphoric acid [11]. The hydrocarbon portion was distilled over a metal cap microcolumn. The experiments were performed in duplicate, and mean values are given in the tables. Results of several typical experiments are given below.

1st Experiment. 6 g of methylphenyltriazene was decomposed in 500 ml of isopropylbenzene. 1510 ml of gas was evolved. The composition of the gas was: methane 36% (yield 55%), nitrogen 64% (yield 97.5%). The following products were isolated from the reaction mixture: a) aniline, 1.35 g (yield 33%), hydrochloride m.p. 194° (mixed sample 193°); b) methylaniline, 1.20 g (yield 25%), hydrochloride m.p. 123° (mixed sample 123°); c) 2,3-dimethyl-2,3-diphenylbutane (dicumyl), 1.8 g (yield 17%), m.p. 119-120° (from methyl alcohol), literature data: m.p. 120° [12].

Found %: M 215, 221. $C_{18}H_{22}$. Calculated M 238.

2nd Experiment. 13.5 g of methylphenyltriazene was decomposed in 900 ml of cyclohexene. 3620 ml of gas was evolved. The composition of the gas was: methane 38.4% (yield 61.3%), nitrogen 61.6% (yield 98.5%). The following products were isolated from the reaction mixture: a) aniline, 5.0 g (yield 54%); b) methylaniline, 1.8 g (yield 17%); c) cyclohexenylamine, 1.0 g (yield 6.0%); b.p. 140-143° at 3 mm.

Found %: N 8.04. M 182, 186; number of double bonds 1.01. $C_{12}H_{17}N$. Calculated %: N 8.00. M 175. Number of double bonds, 1.

d) Dicyclohexenyl, 8.2 g (yield 50%):

B.p. 80.5-81.5 at 4 mm, d_4^{20} 0.9310, n_D^{20} 1.5100, MR_D 52.25. $C_{12}H_{18}$. Calc. 52.28.

Found: M 159, 159; number of double bonds 2.02, 2.00. $C_{12}H_{18}$. Calculated: M 162. Number of double bonds 2.

e) Tercyclohexenyl, 1.0 (yield in %):

B.p. 140-141° at 4 mm, d_4^{24} 0.9930, n_D^{24} 1.5380, MR_D 76.8. $C_{18}H_{24}$. Calc. 77.3.

Found: M 222, 216; number of double bonds 3.03. $C_{18}H_{24}$. Calculated: M 242. Number of double bonds 3.

3rd Experiment. 12 g of benzylphenyltriazene was decomposed in 450 ml of cyclohexene. 1060 ml of gas was evolved. The gas was pure nitrogen (yield 83.0%). The following products were isolated from the reaction mixture: a) aniline, 2.3 g (yield 44%); b) benzylaniline, 3.7 g (yield 35%), hydrochloride m.p. 209-210°.

Found %: N 7.45, 7.60. M 182, 179. $C_{13}H_{13}N$. Calculated %: N 7.65. M 183.

c) Dicyclohexenyl 2.35 g (yield 26%), b.p. 242-245°.

Found: M 161, 158; number of double bonds 1.98. $C_{12}H_{18}$. Calculated: M 162; number of double bonds 2.

d) Dibenzyl, 1.0 g (yield 19%), m.p. 47-48°, mixed sample 47°.

4th Experiment. The decomposition of triazenes in benzene solutions of rubbers was carried out at 120° in all cases, with concentrations: rubber, 3.5% by weight, triazene, 0.66 molar %. The rubber samples were previously extracted with acetone in a Soxhlet apparatus for 4 hours. 1 g of methylphenyltriazene was decomposed in 130 ml of benzene containing 4 g of natural rubber. 205 ml of gas was evolved. The composition of the gas was: nitrogen 77.9% (yield 98.5%), methane 22.1% (yield 27.3%).

Evaluation of vulcanizing power. The compound under investigation was masticated on cold rolls for 5 minutes with a definite amount of natural rubber. Separate 0.7-1.0 g portions of the "hide" formed were heated in nitrogen in sealed ampoules at 120° for different times. A weighed sample of the ampoule contents (~0.35 g) was then extracted with chloroform in a Soxhlet apparatus for 15 hours, after which the weight of the undissolved residue was determined.

* The gas volume is reduced to standard conditions.

** The degree of unsaturation (number of double bonds) was in all cases determined by hydrogenation in ethyl alcohol solution over Pd black.

SUMMARY

1. Propylphenyltriazene, isopropylphenyltriazene, butylphenyltriazene, tert-butylphenyltriazene, allylphenyltriazene, and di(diphenyl)triazene were prepared and described for the first time.
2. The thermal decomposition products of a number of triazenes in isopropylbenzene, cyclohexene, and benzene solutions of rubber were studied.
3. The order of the activities of free radicals in the reaction of H atom removal from various compounds has been established. It was shown that the allyl, crotyl, benzyl, and tert-butyl free radicals practically do not react with isopropylbenzene.
4. It was established that free radicals of low activity (allyl, benzyl, and anilino) do not induce structurization of natural rubber.

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MECHANISM OF THE CATALYTIC ACTION OF ALUMINUM CHLORIDE

IV. KINETICS AND MECHANISM OF THE REACTION OF ALKYLATION OF BENZENE BY OLEFINS

N. N. Lebedev

A great diversity of opinions exists concerning the mechanism of the alkylation of aromatic compounds by olefins. It is known that aluminum chloride catalyzes the addition of hydrogen halides to olefins [1]. The favorable effect of hydrogen halides on the alkylation of benzene by olefins has also been reported [2], which gives reason to suppose that the reaction proceeds through the intermediate formation of a halogenated derivative. However, another explanation appears very plausible, namely that the olefin itself can act as the alkylating agent owing to its power of forming, with aluminum chloride, complexes of the carbonium ion type by means of one of the double bond electron pairs [3]:



An extreme aspect of this viewpoint is the supposition that alkyl halides decompose during the reaction into hydrogen halide and olefins, only the latter being capable of alkylating the aromatic compound [4].

Not one of these opinions is supported by exhaustive proof, which we believed could be found by a study of the kinetics of the reaction.

EXPERIMENTAL TECHNIQUE

Measured volumes of purified benzene, nitrobenzene, and 10% aluminum chloride solutions in nitrobenzene were placed in a reaction flask and 60 ml capacity fitted with a sealed-in bubbler, gas exit tube, and a neck with a ground glass stopper. The required catalyst concentration and composition of the medium was obtained by variations of the amounts added (in all the subsequent experiments the benzene concentration was constant at 12.5%). The flask was placed in a thermostat in which a temperature of $30 \pm 0.05^\circ$ was maintained, and a stream of dry nitrogen was passed for 10 minutes through the reaction mass at a rate of about 60 ml per minute. Cyclohexene, prepared from cyclohexanol [5] (d_4^{20} 0.8110, n_D^{20} 1.4468), containing, according to analytical results [6], 99.13, 99.42% of cyclohexene, was added from a graduated pipet. The first sample was taken at once, after which the stream of nitrogen was stopped. Samples were taken for analysis at definite time intervals, and at those times the stream of nitrogen was reconnected for a short time in order to prevent the access of moisture from the air on removal of the stopper. The sample was transferred quickly with shaking to a flask with dilute hydrochloric acid, and a small excess of 0.1 N bromide-bromate solution was added. The flask was left to stand 15 minutes in the dark, 5 ml of 10% potassium iodide solution was added, and the iodine evolved was titrated by thiosulfate in presence of starch. This analytical technique was verified on previously prepared mixtures of benzene, cyclohexene, and nitrobenzene, and gave good results.

Cyclohexene and benzene in the presence of aluminum chloride give a good yield of phenylcyclohexane, which establishes the basis for the selection of this reaction for the kinetic investigation. However, cyclohexene can not only alkylate benzene by the action of aluminum chloride, but may polymerize [8]. This possibility was verified by keeping cyclohexene in a nitrobenzene solution of aluminum chloride at 30° . Titration of the samples showed that the content of cyclohexene in the solution is rather low in comparison with the value calculated from the amount taken, but remains constant for two hours.

Thus, the interfering effect of polymerization in the experimental conditions described is excluded. The low titration results are to be explained by the addition to the cyclohexene of hydrogen chloride formed by hydrolysis of the catalyst by the moisture remaining in the solvents or adsorbed by the aluminum chloride. This is confirmed by the following facts. When the concentration of the nitrobenzene solution of aluminum chloride was 0.1 mole/liter, the concentration of cyclohexene found was less than the calculated value for the given sample by 0.015 mole/liter, this difference being independent of the cyclohexene concentration. The addition of 0.04 mole/liter of hydrogen chloride (in nitrobenzene solution) to the mixture further decreased the cyclohexene concentration, also

SUMMARY

1. Propylphenyltriazene, isopropylphenyltriazene, butylphenyltriazene, tert-butylphenyltriazene, allylphenyltriazene, and di(diphenyl)triazene were prepared and described for the first time.
2. The thermal decomposition products of a number of triazenes in isopropylbenzene, cyclohexene, and benzene solutions of rubber were studied.
3. The order of the activities of free radicals in the reaction of H atom removal from various compounds has been established. It was shown that the allyl, crotyl, benzyl, and tert-butyl free radicals practically do not react with isopropylbenzene.
4. It was established that free radicals of low activity (allyl, benzyl, and anilino) do not induce structurization of natural rubber.

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by 0.04 mole/liter. Already 0.5 minutes after the mixing, the addition proceeded to completion and no further change of the cyclohexene concentration occurred. This indicates the high rate of the addition reaction between hydrogen chloride and cyclohexene.

Effect of the cyclohexene and aluminum chloride concentrations

Results of experiments in which the effect of cyclohexene and aluminum chloride concentrations on the reaction rate was studied, are shown in Table 1.

Each value given is the mean from several experiments, the number of which is shown in Column 4, while the maximum deviation of the individual results from the mean is shown in Column 5.

TABLE 1

Line No.	Initial cyclohexene concentration, moles/liter	AlCl ₃ concentration, moles/liter	Number of experiments	Deviation, moles/liter	Cyclohexene concentration in moles/liter for reaction times, minutes					Mean rate (moles/liter/minute)
					0.5	10	20	40	60	
1	0.305	0.203	4	±0.005	0.285	0.274	0.261	0.238	0.212	0.00122
2	0.203	0.203	4	±0.003	0.182	0.171	0.159	0.137	0.112	0.00116
3	0.101	0.203	3	±0.003	0.082	0.069	0.059	0.032	—	0.00123
4	0.203	0.100	4	±0.007	0.187	0.180	0.171	0.158	0.139	0.00079
5	0.203	0.049	3	±0.005	0.190	0.188	0.182	0.173	0.163	0.00043

Effect of hydrogen chloride concentration

The effect of hydrogen chloride on the reaction rate was studied by addition of different amounts of hydrogen chloride in nitrobenzene solution to the reaction mass. In these experiments the aluminum chloride concentration was 0.203 mole/liter and the initial cyclohexene concentration, 0.203 mole/liter. The results obtained are shown in Table 2.

TABLE 2

Line No.	Concentration of hydrogen chloride added, moles/liter	Number of experiments	Deviation, moles/liter	Cyclohexene concentration in moles/liter for reaction times, minutes					Mean rate (moles/liter/minute)
				0.5	10	20	30	40	
5	0.02	4	±0.005	0.160	0.135	0.109	0.082	0.052	0.00273
7	0.04	4	±0.004	0.141	0.100	0.057	0.012	—	0.00437
8	0.06	2	±0.004	0.121	0.067	0.014	—	—	0.00562

DISCUSSION OF RESULTS

The experimental results, shown in Fig. 1, indicate that the relationship between the cyclohexene concentration and the reaction time is in all instances expressed by straight lines. Lines 1, 2, and 3 show that their slopes are the same and that therefore the reaction rate does not depend on the cyclohexene concentration.

When hydrogen chloride is added to the reaction mixture, the rate of the process rises considerably, as can be seen by examination of Lines 6, 7 and 8 in comparison with 2 (Fig. 1). The total concentration of hydrogen halide should be equal to the sum of the hydrogen chloride added and that formed as the result of hydrolysis of aluminum chloride by moisture. This sum is equal to the intercept on the ordinate between the initial cyclohexene concentration and the point of intersection with the ordinate of the line for the variation of cyclohexene concentration with time. An examination of the reaction rate and the total hydrogen chloride concentration (Fig. 2) shows that the relationship between them is expressed by a straight line. Thus, the reaction rate is directly proportional to the hydrogen halide concentration:

$$v = k_1[\text{HCl}],$$

It should be pointed out that in all cases the effect of the hydrogen chloride concentration is taken to refer to its concentration before the addition of cyclohexene. During the reaction no hydrogen halide is present in the reaction mass, as it is instantaneously added on to cyclohexene to form cyclohexyl chloride.

A comparison of the Lines 2, 4, and 5 (Figure 1) shows that the reaction rate increases with increase of aluminum chloride concentration, and the ordinate intercepts between the initial cyclohexene concentration (0.203 mole/liter) and the points of intersection of the lines with the ordinate axis are greater with higher aluminum chloride concentrations. This is to be explained by the fact that hydrogen chloride is formed not only by the action of the moisture in the solvents, but also by the action of moisture adsorbed by the solid catalyst used for preparation of the solutions. The hydrogen halide concentrations differed a little in these experiments, being 0.012, 0.015, and 0.020 mole/liter for aluminum chloride concentrations of 0.049, 0.100 and 0.203 mole/liter respectively. With this taken into account, we have the rate constants k_1 equal to 0.036, 0.052, and 0.60 respectively, so that when the aluminum chloride concentration is approximately doubled the reaction rate increases 1.2-1.5 times. This is in agreement with earlier data on the kinetics of the reaction of cyclohexyl chloride with benzene [3], the order of which with respect to the catalyst concentration has an average value of 0.5.

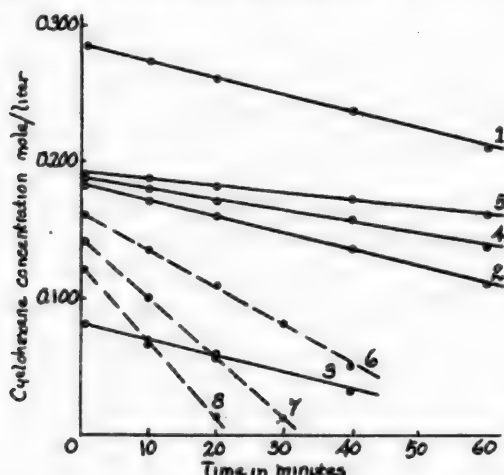


Fig. 1. Numbering as in Tables 1 and 2, latter is the true alkylating agent in the reaction.

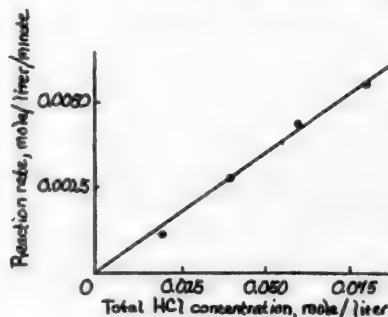


Fig. 2

It is possible to explain only in one way why the reaction rate is independent of the cyclohexene concentration and is directly proportional to the hydrogen chloride concentration. Obviously cyclohexene itself cannot react with benzene, since it does not enter the kinetic equation for the process. The influence of hydrogen chloride should be attributed to its power of adding on to cyclohexene to form cyclohexyl chloride. The



The first of these reactions, as was shown above, proceeds immeasurably rapidly. Therefore free hydrogen chloride is practically absent from the reaction mixture. Having been formed according to Reaction (2), it immediately reacts according to Equation (1). The rate of the process is determined by the last of the reactions given, in which the cyclohexene chloride concentration remains constant and equal to the concentration of hydrogen chloride added to the mixture or formed as the result of hydrolysis of the catalyst by moisture. Thus,

$$v = k_1[\text{RCl}] = k_1[\text{HCl}] = \text{const},$$

where k_1 is the rate constant for the first order reaction between cyclohexyl chloride and benzene.

Calculation of the rate constant for the first order reaction from the data obtained above, by division of the rate by the corresponding total hydrogen chloride concentration, gives the results shown in Table 3.

The last column of this table gives the rate constants k_1' for the reaction between cyclohexyl chloride and benzene, determined earlier [9] by direct measurements of the reaction kinetics in conditions equal to those used in the present study. The close agreement between this constant and the values calculated from data on the kinetics of the reaction between cyclohexene and benzene once again confirms the reaction mechanism assumed.

In our opinion, the reaction mechanism established in the present study is not limited to selected reaction conditions and choice of reagents, but may be generally extended to the alkylation of aromatic compounds by olefins in the presence of aluminum chloride.

TABLE 3

No.	AlCl ₃ concentra- tion (moles/liter)	Hydrogen chloride concentra- tion moles/liter	Reaction rate (moles/liter/ minute)	Rate con- stant k_1 min ⁻¹	k_1' min ⁻¹
1	0.203	0.020	0.0012	0.060	} 0.0642
2	0.203	0.040	0.00273	0.068	
3	0.203	0.060	0.00437	0.073	
4	0.203	0.080	0.00552	0.069	
5	0.100	0.015	0.00079	0.052	0.0470
6	0.049	0.012	0.00043	0.036	0.0308

SUMMARY

1. The rate of the reaction between cyclohexene and benzene in the presence of aluminum chloride is a constant value which does not depend on the reaction time or the cyclohexene concentration, but is directly proportional to the aluminum chloride concentration.

2. In the reaction between olefins and aromatic compounds in the presence of aluminum chloride the actual alkylating agent is the alkyl halide formed by the addition of hydrogen halide to the olefin.

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II. EXCHANGE REACTIONS IN THE INTERACTION OF HALOGENATED NAPHTHALENES WITH HYDROGEN HALIDES

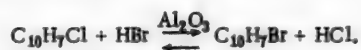
N. N. Vorozhtsov, Jr., and N. M. Przhivalgovskaya

For the elucidation of the isomerization mechanism of halogen derivatives of naphthalene it appeared of interest to study the reaction between 1-bromo-naphthalene and hydrogen chloride, and 1-chloronaphthalene and hydrogen bromide, over aluminum oxide in the vapor phase (at 350°).

In the present study it was established that, in these conditions, isomerization of halogenated naphthalenes is accompanied by a halogen exchange reaction: bromonaphthalene is partially converted into chloronaphthalene, and conversely*. Here and subsequently the terms chloronaphthalene and bromonaphthalene are applied to the isomeric mixtures of the corresponding halogenated naphthalenes.

A study of the literature on the subject showed that similar exchange reactions have been described only for compounds in which the halogen atoms have considerable mobility and can in general be easily replaced by various atoms or groups. These include, for example, organic acid chlorides [1], di- and trinitrochlorobenzene [2, 3], and 2,3,5,6-tetrabromomethylquinol [4].

Investigation of the exchange reaction in halogenated derivatives in the aromatic series over aluminum oxide at 350° showed that the conversion of chloronaphthalene by the action of hydrogen bromide into bromonaphthalene and hydrogen chloride is a reversible reaction:

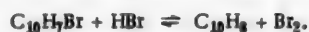


Isomerization takes place simultaneously with the exchange reaction, and in consequence the reaction product contains both isomers, both of chloro- and bromonaphthalene.

The equilibrium proportions of the chloro and bromo derivatives are determined by the proportions of the starting substances. With the use of 5-6 moles of hydrogen bromide per 1 mole of 1-chloronaphthalene and 9-10 moles of hydrogen chloride per 1 mole of 1-bromonaphthalene, the halogen exchange in halogenated naphthalenes practically reaches 100% (see Figure).

The presence of a catalyst (aluminum oxide) is a necessary condition for the reaction. Without the catalyst, exchange (and isomerization) does not take place.

The exchange reaction, both in chloro- and in bromonaphthalene, is accompanied by the formation of naphthalene and its dihalogen derivatives. This may be explained by the fact that in both cases bromonaphthalene and hydrogen bromide are always present in the system. Naphthalene and its dihalogen derivatives are formed in consequence of the reversible nature of the reaction of naphthalene bromination [5]:

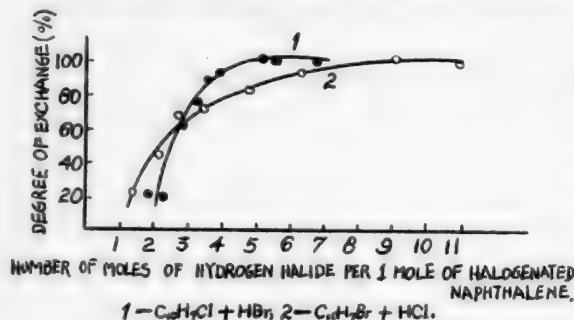


The reversibility of the bromination reaction was first established by Faborsky in relation to bromine derivatives of the aliphatic series [6].

In order to determine the possibility of bringing about the exchange reaction in the benzene series, we carried out several experiments on the reaction of chlorobenzene with hydrogen bromide and of bromobenzene with hydrogen

* The first experiments to establish the existence of this exchange reaction were performed by E. P. Fokin in 1951.

chloride. It was established that no halogen exchange takes place between chlorobenzene and hydrogen bromide at 400° over aluminum oxide. Under the same conditions bromobenzene is converted into chlorobenzene with 29.2% yield with a molar ratio of 1:7.3 between the bromobenzene and hydrogen chloride.



Attempts to replace chlorine or bromine atoms in aromatic compounds by fluorine by passing a monohalogenated naphthalene over aluminum oxide at 350° in the presence of hydrogen fluoride were not successful. It is interesting to note that fluorinated naphthalenes, on the contrary, exchange fluorine for chlorine fairly readily by the action of hydrogen chloride on them. For example, 1-fluoronaphthalene is converted into chloronaphthalene with 22.8% yield when fluoronaphthalene is passed with 4.13 moles of hydrogen chloride, while 2-fluoronaphthalene is converted into chloronaphthalene in 40.2% yield by the action of 3.75 moles of hydrogen chloride.

Thus, only hydrogen chloride and bromide take part in exchange reactions between halogenated naphthalenes and hydrogen halides over aluminum oxide. The exchange reaction does not take place with hydrogen fluoride.

In the course of the work it was established that the aluminum oxide used as catalyst reacts with HF at 350°, and is almost completely converted into AlF_3 .

Analogous experiments with HCl showed that chemical action also takes place in this case. The activation of aluminum oxide by hydrogen chloride always results in the formation of a small amount of water and an increase of 1.7-1.9% in the weight of the catalyst.

Quite probably when the catalyst is treated with HCl (or HBr) the hydroxyl groups contained in it are replaced by halogen atoms with the formation of water. As the result of this reaction, $Al-Cl$ groups appear on the catalyst surface, and these apparently act as the active centers.

EXPERIMENTAL

The experiments with hydrogen chloride or bromide were carried out in a quartz tube 1 meter long with 17 mm internal diameter. The tube was heated in an electric furnace 80 cm long, fitted with a contact thermometer and a relay, so that the desired temperature could be maintained to an accuracy of $\pm 3^\circ$. The catalyst used was technical active aluminum oxide which was activated before the start of the experiments by dry hydrogen halide for 1.5 hours at the experimental temperature of 350°. The volume occupied by the catalyst was as a rule 68-70 ml. Otherwise the experimental technique did not differ from that described previously [7].

The experiments with hydrogen fluoride were carried out in a steel tube. The amount of hydrogen fluoride passed was determined by the loss of weight of the HF cylinder. The rate of flow of the hydrogen fluoride was controlled by the number of bubbles in a polystyrene wash bottle sealed by vaseline oil.

The catalyzate was neutralized by dry soda and filtered, and then investigated. The course of the conversion was determined from the distillation results.

The 2-isomer content in the monochloro- and monobromonaphthalene fractions was determined from the solidification curves for binary mixtures of 1- and 2-isomers [5, 8].

When the exchange reaction took place, the degree of halogen substitution was determined by analysis of the acid gases leaving the reaction tube. The mixture of hydrogen fluoride with the chloride or bromide was analyzed argentometrically [9]. In the analysis of mixtures of hydrogen chloride and bromide, the difference between the densities of aqueous solutions of these gases at the same concentrations was used. Data for aqueous solutions of hydrogen bromide [10] and chloride [11] were used to plot $c = f(d)$ graphs, where c is the molar concentration and d the density of the solution. The molar composition of the mixture was determined graphically from the concentration of the solution and its density. The method was checked with synthetic mixtures of HCl and HBr. The relative error was $\pm 3\%$ for 10-90% molar concentrations of HCl.

Conversion of 1-chloronaphthalene into bromonaphthalenes

0.85 mole (138 g) of 1-chloronaphthalene and 1-chloronaphthalene and 1.12 mole of hydrogen bromide was

passed over aluminum chloride in 4 cycles of 3 hours each. Distillation of the catalyzate (137.5 g) yielded the following fractions: 1st, b.p. 215-220°, 21.7 g, solidif. p. 76.9°; 2nd, b.p. 220-256°, 4.7 g; 3rd, b.p. 256-263°, 41.6 g, solidif. p. 15.2°; 4th, b.p. 263-276°, 25.7 g; 5th, b.p. 277-283°, 9.2 g, solidif. p. 10.4°; residue 53 g.

The main fractions: 1st, 3rd, 5th, and the residue, were studied.

The 1st fraction in its constants corresponded to naphthalene. The amount of naphthalene (given here and subsequently as the sum of the weights of the 1st and 50% of the 2nd fractions) was 24.0 g (0.188 mole) or 22.1% molar on the 1-chloronaphthalene passed.

The 3rd fraction corresponded to the original monochloronaphthalene by its boiling point. When the fraction was cooled to 0°, a crystalline product was obtained from it, which after three recrystallizations from methanol formed shiny leaflets, m.p. 55-56°.

Found %: C 74.07, 74.13; H 4.48, 4.39. $C_{10}H_7Cl$. Calculated %: C 73.86; H 4.31.

The analytical data, and boiling and melting points of this substance agreed with those of 2-chloronaphthalene, while the fraction itself was a mixture of monochloronaphthalenes (with 47% of the 2-isomer).

The 5th fraction. When this was cooled to 0°, and filtered, a crystalline product was obtained, which melted at 54-55° after three recrystallizations from methanol. It formed white leaflets with a nacreous luster. The literature gives m.p. 56, 57, 58 and 59° [12] for 2-bromonaphthalene.

Found %: C 58.49, 58.43; H 3.44, 3.55. $C_{10}H_7Br$. Calculated %: C 58.00; H 3.41.

A mixed sample of this compound with 2-bromonaphthalene gave no melting point depression. However, the melting point was not depressed in a mixture with 2-chloronaphthalene either. According to literature data [12], 2-chloronaphthalene forms mixed crystals with 2-bromonaphthalene, and therefore, a mixture of the two shows no melting point depression [14]; therefore subsequently mixed sample melting points were not determined for the identification of these compounds.

A picrate with m.p. 78-79° was obtained from the compound. According to the literature, the melting point of 2-bromonaphthalene picrate is 79° [15].

The elementary composition of the mother liquor was also determined.

Found %: C 58.37, 58.25; H 3.49, 3.40. $C_{10}H_7Br$. Calculated %: C 58.00; H 3.41.

By its boiling point and elementary composition, the 5th fraction was a mixture of monobromonaphthalenes (with 48.5% of the 2-isomer).

The residue on cooling yielded a crystalline substance which melted at 155-156.5° after three recrystallizations from methanol. It formed white leaflets with a nacreous luster.

Found %: C 41.83, 41.92; H 2.25, 2.30. $C_{10}H_6Br_2$. Calculated %: C 42.00; H 2.12.

By its melting point and analytical data the compound corresponded to 2,6-dibromonaphthalene. The literature give m.p. 158° [16], 160° [17]. A mixed sample of this compound with known 2,6-dibromonaphthalene gave no melting point depression.

Reaction of 1-chloronaphthalene with hydrogen bromide in absence of catalyst. 18.4 g (0.113 mole) of 1-chloronaphthalene and 0.62 mole of hydrogen bromide was passed for 4 hours through a reaction tube filled with pieces of pumice previously treated with hydrochloric acid. The yield of catalyzate was 17.82 g (97%). The reaction product distilled completely in the range 254-259° (753 mm), n_D^{20} 1.6304, and was thus the original 1-chloronaphthalene.

Conversion of 1-bromonaphthalene into chloronaphthalenes

1-Bromonaphthalene was prepared by bromination of naphthalene [18]. The fraction used for the investigation had b.p. 275-280° (752 mm), solidif. p. +2°, n_D^{20} 1.6570, d_4^{20} 1.4915, content of the 2-isomer 3%.

0.196 mole (40.5 g) of 1-bromonaphthalene and 0.64 mole of hydrogen chloride was passed over aluminum oxide for 4 hours. Distillation of the catalyzate (31.2 g) yielded the following fractions: 1st, b.p. 215-220°, 4.8 g solidif. p. 76.3°; 2nd, b.p. 220-256°, 1.6 g; 3rd, b.p. 256-263°, 2.9 g solidif. p. 16.1°; 4th, b.p. 263-275°, 2.7 g; 5th, b.p. 275-282°, 2.5 g solidif. p. 10.2°; 6th, b.p. 285-305°, 4.0 g; residue 2.4 g.

The main fractions: 1st, 3rd, 5th and 6th, were investigated.

The 1st fraction was naphthalene. M.p. 77-79°. The amount of naphthalene was 5.6 g, or 22.4% molar of the 1-bromonaphthalene passed.

The 3rd fraction on cooling yielded a crystalline substance which melted at 55-56° after three recrystallizations from methanol.

Found %: C 73.93, 74.07; H 4.31, 4.49. $C_{10}H_7Cl$. Calculated %: C 73.86; H 4.31.

The boiling and melting point and the elementary composition of the substance showed it to be 2-chloronaphthalene. For identification, the picrate was prepared from the substance. This formed yellow needles, m.p. 80.3-81°. According to the literature the melting point of 2-chloronaphthalene picrate is 81.5° [15].

The liquid part of this fraction was separated into 3 fractions under vacuum. The middle fraction, b.p. 127° (12 mm) was analyzed.

Found %: C 73.26, 73.01; H 4.47, 4.62. $C_{10}H_7Cl$. Calculated %: C 73.86; H 4.31.

Therefore the 3rd fraction was a mixture of monochloronaphthalenes.

The 5th fraction on cooling yielded a crystalline product which melted at 56.2-57.1° after three recrystallizations from methanol. The picrate prepared from this compound melted at 78.2-78.9°. According to the literature, the melting point of 2-bromonaphthalene picrate is 79° [7]. The 5th fraction was a mixture of monobromonaphthalenes (with 48.5% of the 2-isomer).

The 6th fraction was separated by suction on a funnel into a crystalline substance and a liquid. The crystalline substance was recrystallized twice from methanol. It formed shiny leaflets, m.p. 137-139°.

Found %: C 49.51, 49.70; H 2.65, 2.52. $C_{10}H_6BrCl$. Calculated %: C 49.80; H 2.48.

By its composition, this substance was chlorobromonaphthalene. Several chlorobromonaphthalenes are described in the literature, but none corresponds to the melting point found. By analogy with the previous experiment we may assume that the compound is 2,6-chlorobromonaphthalene (not described in the literature). The liquid part of the fraction was not investigated.

Effect of the proportions of hydrogen bromide and 1-chloronaphthalene on the degree of halogen exchange. In this series of experiments the volume occupied by the catalyst was 100 ml. The molar ratio of 1-chloronaphthalene and hydrogen bromide was varied after every hour. The contact time varied in very wide limits (70-200 sec.), but all the experiments were carried out in a region far from the kinetic region, and therefore these variations could not affect the results. The experimental results are collected in Table 1 and shown in the Figure (Curve 1).

Effect of the proportions of hydrogen chloride and 1-bromonaphthalene on the degree of halogen exchange. The experiments were carried out in the same conditions as previously. The results are shown in Table 2 and in the Figure (Curve 2).

Reaction of chlorobenzene with hydrogen bromide. 14.1 g (0.125 mole) of chlorobenzene and 0.48 mole of hydrogen bromide was passed over aluminum oxide in 3 hours at 400°. The yield of catalyzate was 72 g (97.4%). The product distilled completely at 132-133° (755 mm), d_4^{20} 1.108, n_D^{20} 1.5263. The original chlorobenzene: d_4^{20} 1.108, n_D^{20} 1.5257.

Reaction of bromobenzene with hydrogen chloride. 45.9 g (0.292 mole) of bromobenzene and 2.14 moles of hydrogen chloride was passed in 2 cycles of 5 hours each over the catalyst at 400°. The yield of catalyzate was 40.2 g (87.7%). The product was distilled over a column 30 cm high and 12 mm internal diameter. The following fractions were obtained: 1st, b.p. 130-133°, 7.6 g, d_4^{20} 1.1073, n_D^{20} 1.5255; 2nd, b.p. 133-150°, 4.1 g, n_D^{20} 1.5471; 3rd, b.p. 150-155°, 20.8 g, d_4^{20} 1.4942, n_D^{20} 1.5597.

For identification of the 1st fraction, containing chlorobenzene, 1 g was nitrated by means of nitric acid [19] to the dinitro derivative. After recrystallization from dilute ethanol, yellow needle-like crystals with m.p. 50° were obtained. The literature gives m.p. 53° for dinitrochlorobenzene. No melting point depression was found in a mixed sample with known 2,4-dinitrochlorobenzene.

Reaction of 1-chloronaphthalene with hydrogen fluoride. 18 g (0.110 mole) of 1-chloronaphthalene and 18 g (0.9 mole) of hydrogen fluoride was passed over the catalyst in 3.5 hours at 350°. The yield of catalyzate was 14.59 g (81%).

TABLE 1

Experiment No.	Working period	Consumption of 1-chloronaphthalene (in moles)	HBr flow rate (ml/min)	Molar ratio of HBr to 1-chloronaphthalene	Amount of HCl formed (moles)	Degree of halogen exchange in 1-chloronaphthalene (in molar %)
1	I	0.0210	28	3.57	0.0185	88.2
	II	0.0251	21	2.24	0.0048	19.3
	III	0.0229	48	5.62	0.0228	100.0
2	I	0.0253	26	2.76	0.0158	62.4
	II	0.0310	21	1.82	0.0064	20.6
	III	0.0295	43	3.90	0.0275	93.0
3	I	0.0310	38	3.26	0.0232	74.8
	II	0.0274	54	5.27	0.0275	100.0
	III	0.0288	73	6.77	0.0263	98.0

TABLE 2

Experiment No.	Working period	Consumption of 1-bromonaphthalene (in moles)	HCl flow rate (ml/min)	Molar ratio of HCl to 1-bromonaphthalene	Amount of HBr formed (moles)	Degree of halogen exchange in 1-bromonaphthalene (in molar %)
1	I	0.0450	36	2.14	0.0191	42.4
	II	0.0536	54	2.70	0.0354	66.1
	III	0.0565	73	3.45	0.0401	71.0
	IV	0.0530	94	4.76	0.0434	81.9
2	I	0.0550	28	1.36	0.0118	21.4
	II	0.0276	65	6.30	0.0255	92.5
	III	0.0254	86	9.06	0.0253	100.0
	IV	0.0268	110	11.0	0.0259	97.0

The product distilled at 252-257° (749 mm) and solidified at -1°. To show the presence of fluorinated derivatives in the reaction products, about 50 mg of the substance was fused with 3 times the amount of metallic potassium in a steel bomb [20]. A negative result was given by the qualitative reaction for fluorine with zirconium oxychloride in the presence of sodium alizarin sulfonate, which showed that no exchange reaction took place between chloronaphthalene and hydrogen fluoride.

The solidification point of the reaction product (-1°) corresponds to 33.3% content of 2-chloronaphthalene. When 1.56 g of 2-chloronaphthalene was added to 1.35 g of the product, the mixture solidified at 35.7°, which corresponds to 70% content of the 2-isomer. It was found by calculation that the original product contained 34% of 2-chloronaphthalene. The close agreement between the values found by the two determinations indicates once again that the reaction product was a mixture of monochloronaphthalenes only.

When the aluminum oxide was activated by hydrogen fluoride before the experiment, water was evolved. After the experiment the catalyst gained 60% in weight, lost its mechanical strength, and could not be regenerated. The composition of the catalyst indicated that it was almost completely converted into aluminum fluoride.

Found %: Al 36.3, 36.4; F 61.02, 58.20. AlF_3 . Calculated %: Al 32.12; F 67.88.

Reaction of 1-bromonaphthalene with hydrogen fluoride. 34.8 g (0.167 mole) of 1-bromonaphthalene and 33 g (1.65 mole) of hydrogen fluoride was passed over the catalyst in 3 hours at 350°. The following fractions were collected during distillation of the catalyzate: 1st, b.p. 230-279°, 1.59 g, solidif. p. 33°; 2nd, b.p. 279-282°, 20.46 g, solidif. p. 7°. The gases leaving the reaction tube contained 0.0196 mole of hydrogen bromide. The 1st fraction was analyzed for fluorine content, by fusion of 70 mg of the substance with metallic potash in a steel bomb. A qualitative test of the melt by means of zirconium oxychloride gave a negative result, which indicated the absence of any exchange reaction between bromonaphthalene and hydrogen fluoride. The 2nd fraction contained 45.6% of the 2-isomer.

Reaction of 1-fluoronaphthalene with hydrogen chloride. 1-Fluoronaphthalene* prepared by the Balz and Schinemann method [22], had b.p. 216.3° (754 mm), solidif. p. -10.5°, n_D^{20} 1.5933.

Experiment 1. 28.3 g (0.18 mole) of 1-fluoronaphthalene and 20.2 g (0.56 mole) of hydrogen chloride was passed over aluminum oxide in 3 hours. Distillation of the catalyzate (20.9 g) yielded the following fractions (at 748 mm): 1st b.p. 213-214.5°, 14.7 g, n_D^{20} 1.5933 (1-fluoronaphthalene); 2nd, b.p. 218.5-251°, 1.8 g, n_D^{20} 1.6048 (intermediate fraction); 3rd, b.p. 253.4-254.5°, 2.4 g, n_D^{20} 1.6300 (monochloronaphthalene).

Experiment 2. The preceding experiment was repeated in order to determine the degree of conversion of 1-fluoronaphthalene into chloronaphthalene. 19.90 g (0.136 mole) of 1-fluoronaphthalene and 20.2 g (0.56 mole) of hydrogen chloride was passed over the catalyst. The catalyzate was distilled in the range 215-256° (756 mm). Yield 17.6 g.

63.10 mg sub.: 5.79 mg F; 3.62 mg Cl. Found %: $\text{C}_{10}\text{H}_7\text{Cl}$ 26.3; $\text{C}_{10}\text{H}_7\text{F}$ 75.0.

According to the analytical data, the reaction product contained 13.2 g (0.096 mole) of 1-fluoronaphthalene and 4.4 g (0.0270 g mole) of chloronaphthalene; hence the exchange of fluorine for chlorine proceeded to 22.8 molar %.

Reaction of 2-fluoronaphthalene with hydrogen chloride. 2-Fluoronaphthalene, prepared analogously to 2-fluoronaphthalene [23], had b.p. 217.8° (750 mm), solidif. p. 59.3°, m.p. 60.2-60.7°.

22.6 g (0.15 mole) of 2-fluoronaphthalene and 20.2 g (0.56 mole) of hydrogen chloride was passed over aluminum chloride in 3 hours. The following fractions were collected (at 750 mm) by distillation of the catalyzate (20.2 g) from an ordinary Wurtz flask: 1st, b.p. 216.5-219.5°, 2.7 g, solidif. p. 55.7° (2-fluoronaphthalene); 2nd, b.p. 220.5-250°, 10.8 g, solidif. p. 51.8° (intermediate fraction); 3rd, b.p. 252.5-256.5°, 3.5 g, solidif. p. 48.5° (monochloronaphthalene); residue 3.0 g.

The fluorine and chlorine contents of the 1st, 2nd, and 3rd fractions were determined (Table 3).

TABLE 3

Fraction	Weight taken (in mg)	Found		Found			
		F	Cl	$\text{C}_{10}\text{H}_7\text{F}$		$\text{C}_{10}\text{H}_7\text{Cl}$	
				(mg)	(%)	(mg)	(%)
1st	73.33	8.95	0.966	68.79	93.80	4.43	6.04
2nd	60.46	4.97	4.93	38.20	63.20	22.60	37.40
3rd	85.67	1.35	16.61	10.58	12.11	76.21	88.80

The following chloronaphthalene contents were calculated for the fractions from the analytical data: 1st, 0.166 g, 2nd, 4.04 g, 3rd, 3.11 g. Thus, the 3 fractions contained 9.73 g (0.0666 mole) of 2-fluoronaphthalene and 7.32 g (0.0449 mole) of chloronaphthalene, whence it follows that fluorine was exchanged for chlorine in 2-fluoronaphthalene by 40.2 molar %.

Reaction of aluminum oxide with hydrogen chloride. Active aluminum oxide in the form of a finely ground powder was placed in a test tube with a ground glass stopper and then put into a quartz tube heated in an electric furnace. The furnace temperature was measured by means of a thermocouple. The catalyst in the open test tube

* The monofluoronaphthalenes were prepared by K. K. Babievsky; he also carried out the experiments on the reactions between monofluoronaphthalenes and hydrogen chloride.

was dried in the tube in a stream of dry carbon dioxide at 350° to constant weight, and then subjected to the action of dry HCl. Hydrogen chloride was passed for 1 hour at the same temperature, and was then displaced from the tube by dry carbon dioxide to a negative reaction for hydrogen chloride. The test tube with the catalyst was weighed. The percentage increase in the dry weight of the catalyst was 1.71 and 1.92 (in two experiments).

An aqueous extract of the catalyst treated with HCl and then with CO₂ gave a copious white precipitate with silver nitrate solution.

SUMMARY

1. It was established that halogenated naphthalenes enter halogen exchange reactions with hydrogen chloride and bromide over aluminum oxide at 350°. 1-Chloronaphthalene was converted into bromonaphthalenes, and 1-bromonaphthalene and 1- and 2-fluoronaphthalenes into chloronaphthalenes.

2. Simultaneously with the halogen exchange, isomerization of the halogenated derivative takes place (as a result of which the reaction product contains both isomers of the monohalogenated derivative), and also conversion of part of the monohalogen derivative into naphthalene and polyhalogen derivatives.

3. Hydrogen fluoride does not enter into an exchange reaction with 1-chloro- and bromonaphthalene. Therefore the reaction between fluoronaphthalene and hydrogen chloride is irreversible, unlike the reaction between bromonaphthalene and hydrogen chloride.

4. The possibility of converting bromobenzene into chlorobenzene by the action of hydrogen chloride has been demonstrated.

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INVESTIGATION OF THE CATALYTIC CONVERSION OF ALCOHOLS INTO

HYDROCARBONS OF THE DIVINYL SERIES

XVII. HEPTADIENE-1,3 AND HEPTADIENE-2,4 FROM A MIXTURE OF n-BUTYL ALCOHOL AND ACETONE

Yu. A. Gorin and F. A. Vasilyeva

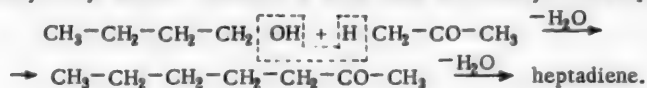
A series of earlier papers described the formation of hydrocarbons with conjugate double bond systems from binary mixtures of various alcohols with carbonyl compounds by the action of Lebedev's catalyst, used in the preparation of divinyl from ethyl alcohol [1].

The addition of acetaldehyde to the ethyl alcohol increased the yield of divinyl calculated on the reacted alcohol [2], a mixture with acetone yielded piperylene [3], a mixture with methyl ethyl ketone gave hexadiene-2, 4 [4], a mixture of isobutyl alcohol with acetaldehyde gave 2-methylpentadiene-2,4 [5], a mixture of n-butyl alcohol with acetaldehyde gave hexadiene-2,4 [6], and a mixture of methyl alcohol with acetone, and also a mixture of isopropyl alcohol with formaldehyde, gave divinyl [7].

The formation of diethylenic hydrocarbons from mixtures of alcohols with carbonyl compounds with the use of aluminum oxide as catalyst was also observed by other workers. Ostromyslensky obtained divinyl from an equimolecular mixture of alcohol with acetaldehyde over this catalyst [8], and piperylene from mixtures of isopropyl or n-propyl alcohol with acetaldehyde [9].

Weizmann and Garrard [10] passed a mixture of n-butyl alcohol and acetone over aluminum oxide at 350°, and found heptadiene, methyl amyl ketone, and small amounts of butyraldehyde and isopropyl alcohol, in the reaction products.

They attributed the formation of heptadiene to direct intermolecular dehydration of n-butyl alcohol and acetone, giving rise to methyl amyl ketone. Removal of water from the latter yielded heptadiene:



These authors did not establish the structure of the heptadiene or a scheme for its formation.

We investigated the conversion of a mixture of n-butyl alcohol with acetone over Lebedev's catalyst, and found that the reaction products contained the diethylenic hydrocarbons C_7H_{12} , consisting of a mixture of heptadiene-1,3 and heptadiene-2,4 in a ratio of 2:1. The yield of C_7H_{12} hydrocarbons was 3.5% by weight, calculated on the sum of the reacted n-butyl alcohol and acetone.

In addition to the C_7H_{12} hydrocarbons, C_6 and C_8 hydrocarbons, and also butyraldehyde and isopropyl alcohol were found. Propylene and butylene were found in the gaseous products.

We explain the formation of heptadienes of the above structure on the basis of the principles of a scheme for the formation of divinyl from ethyl alcohol, which was put forward and experimentally established in a series of earlier papers by one of the present authors [11, 12, 13].

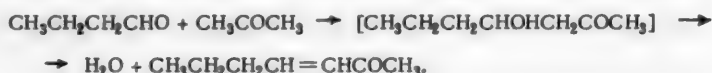
We assume that the conversion of other alcohols by the action of Lebedev's catalyst, and also of binary mixtures of various alcohols and of binary mixtures of alcohols with carbonyl compounds, into hydrocarbons with conjugated double bond systems, follow the same mechanism [13]. These reactions are based on condensation of carbonyl compounds, which are either formed by dehydration of the original alcohols, or are introduced in mixtures with the various alcohols. The condensation is accompanied by the removal of water and the formation of unsaturated aldehydes or unsaturated ketones, according to the nature of the alcohols or carbonyl compounds used. Subsequent conversions of the condensation products by reduction to unsaturated alcohols followed by dehydration lead to the formation of hydrocarbons with conjugated double bond systems.

The formation of heptadienes from a mixture of n-butyl alcohol with acetone may be represented by the following scheme.

1. Conversion of n-butyl alcohol into butyraldehyde by the action of the dehydrogenating component of the catalyst



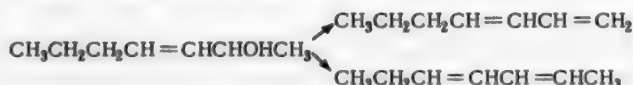
2. Condensation of butyraldehyde with acetone to give butylideneacetone*



3. Reduction of butylideneacetone by butyl alcohol to an unsaturated secondary alcohol



4. Dehydration of the secondary alcohol, accompanied by a regrouping of the double bonds and the formation of two isomers - heptadiene-1,3 and heptadiene-2,4



It is possible that (I) is the primary dehydration product, which isomerizes to the more stable (II) with a conjugate system in the middle of the carbon chain. Examples of similar reactions have been described by Prevost [14] and Dumoulin [15].

5. The formation of isopropyl alcohol is explained by the reduction of acetone by butyl alcohol



The dehydration of the original butyl alcohol, and also of the isopropyl alcohol formed, results in the formation of butylene and propylene, found in the gaseous reaction products.

The C_8 hydrocarbons are formed by the condensation of two molecules of acetone [16], and the C_9 hydrocarbons by the condensation of two molecules of butyraldehyde [17]. These hydrocarbons were not investigated in detail in the present work.

Small amounts of heptadiene were found among the by-products of divinyl production from ethyl alcohol by Lebedev's method [18]. The results of the present study explain its formation in this process. It is known that, in addition to divinyl, butyraldehyde, acetone, and butyl alcohol are formed as by-products. Interaction of these substances and their subsequent conversion by the action of Lebedev's catalyst should lead to the formation of heptadienes with the structure shown above.

It should be pointed out that the formation of a diene hydrocarbon by dehydration of methyl amyl ketone over Al_2O_3 according to Weizmann and Garrard's scheme [10] seems improbable. If such a reaction took place, the evidently divinyl could be obtained from methyl ethyl ketone by dehydration over Al_2O_3 . However, such a reaction is not known.

It follows from Weizmann and Garrard's data that in their experiments acetone was reduced by butyl alcohol with the formation of isopropyl alcohol and butyraldehyde. The reduction of carbonyl compounds by alcohols through hydrogen redistribution, which occurs in the conditions of Lebedev's process [11, 13, 18], also apparently takes place under the influence of aluminum oxide which was used by Weizmann and Garrard; therefore the butylideneacetone formed by the action of Al_2O_3 from acetone and butyraldehyde should be reduced to an unsaturated secondary alcohol, which could subsequently be completely dehydrated to heptadiene.

The formation of methyl amyl ketone observed by Weizmann and Garrard is the result of intramolecular regrouping which may occur in the unsaturated secondary alcohol formed in the intermediate stage by the reduction of butylideneacetone by butyl alcohol



Similar isomerization by the action of aluminum oxide was studied by Weston and Adkins [19] in the case of allyl alcohol, which was thereby converted into propionic aldehyde.

* It must be pointed out that Weizmann and Garrard found butylideneacetone in the reaction products when a mixture of butyraldehyde with acetone was passed over aluminum oxide at 350°.

Thus, by means of our proposed scheme it is possible to explain all the reactions observed by Weizmann and Gerrard with the closest approach to reality.

EXPERIMENTAL

n-Butyl alcohol (b.p. 116.8-117.8°, d_4^{20} 0.8019, n_D^{20} 1.3985) and acetone (b.p. 56-57°, d_4^{20} 0.7915, n_D^{20} 1.3582), were used.

In order to determine the conditions favoring the formation of C_7 diethylenic hydrocarbons, preliminary experiments were carried out with mixtures of butyl alcohol and acetone (1:1 and 1:2 molar) over mixed Lebedev's catalysts, containing the dehydrogenating and dehydrating components in different proportions. The experiments were carried out with the aid of the tubular furnace described earlier [20]. 200 ml of the catalyst was placed in the furnace. The highest yields of hydrocarbons with conjugate double bond systems (as shown by the formation of a white precipitate of polymer sulfone by the action of SO_2) were found with the use of a catalyst of modified composition (increased dehydrogenating and decreased dehydrating component contents) at 380° and with a 1:1 molar ratio of n-butyl alcohol to acetone.

A series of experiments was carried out in order to accumulate the reaction products under the conditions chosen. In each of these experiments a mixture of n-butyl alcohol and acetone was passed through the furnace in 200 ml portions at a rate of 1 ml per minute. After the experiment the catalyst was regenerated by air for 1 hour at 525°. A portion of gas was collected in each experiment to make up an average sample. The liquid products were combined; the hydrocarbons were separated from the aqueous layer and washed with water, to remove unreacted butyl alcohol and other soluble products, to constant volume. The aqueous layer and the wash waters were combined and n-butyl alcohol, acetone, and other reaction products were obtained from them by distillation.

A total amount of 1920 g of mixture (1068 g of n-butyl alcohol and 852 g of acetone) was passed. 343.5 g of butyl alcohol and 305 g of acetone was returned unchanged. 531.2 g of water-insoluble products was obtained. The total yield of washed hydrocarbons was 27.8% by weight calculated on the mixture passed, and 41.8% by weight on the sum of the reacted n-butyl alcohol and acetone (1271.5 g).

Investigation of the Reaction Products

a) The average gas sample had the following composition (in vol %): CO_2 -7.7; CO-0.61; H_2 -22.8; C_3H_6 -25.5; C_4H_8 -38.2 (propylene and butylene were determined by distillation over a Podbelniak type column).

b) The fraction up to 99° was distilled from the combined aqueous solution. The upper layer of the distillate was separated off, and the lower aqueous layer was salted out by potash; the upper layer which separated out was combined with the previous one. The product was dried by potash and distilled over a column. The following fractions were collected: 1st, b.p. 56-58° (acetone), d_4^{20} 0.793; 2nd, b.p. 73-80° (butyraldehyde), d_4^{20} 0.818; 3rd, b.p. 82-84.5° (isopropyl alcohol), d_4^{20} 0.791; 4th, b.p. 115-116° (butyl alcohol), d_4^{20} 0.811.

Acetone was determined by Chelintsev's method [21] with the aid of furfural after preliminary oxidation of the aldehydes by moist silver oxide [22]. The presence of butyraldehyde was proved by the preparation of 2,4-dinitrophenylhydrazone with m.p. 120.5° (122° according to the literature). Isopropyl alcohol was identified by the preparation of isopropyl acetate: the boiling point and the density of the ester obtained agreed with the literature data.

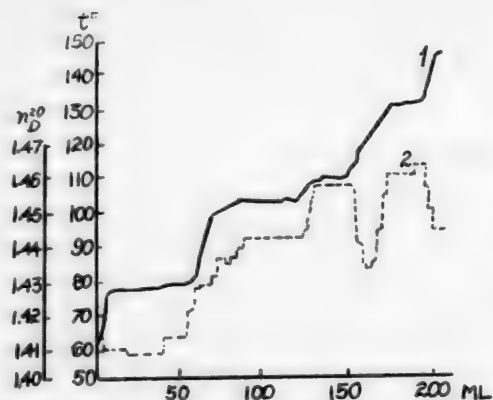
The upper condensate layer, in 531.2 g yield after being washed to constant volume, was dried with calcium chloride, boiled 8 hours over sodium, and distilled in a nitrogen atmosphere from a flask with a double bulb dephlegmator. 457.3 g was used for the distillation.

The following fractions were obtained: 1st, b.p. 56-90°, 6.6%; 2nd, b.p. 90-110°, 23.4%; 3rd, b.p. 110-126°, 22.2%; residue and losses, 47.8%.

The 2nd and 3rd fractions were combined and distilled over a metal cap column (50 theoretical plates).

The distillation results are shown in the figure, which, in addition to the distillation curve, shows refractometric data (the abscissa axis shows the amount of the fractions in milliliters, and the ordinate axis, the boiling points and n_D^{20}).

As the figure shows, the distillation yielded 4 fractions, corresponding to hydrocarbons of different compositions: 77-78°- C_6 ; 103-103.6° and 109.2-109.7°- C_7 ; 132-133°- C_8 .



Hydrocarbon distillation curves.

1) Distillation curve, 2) refraction curve.

Investigation of the 103-103.6° fraction

By its boiling point this fraction was close to heptadiene-1,3.

n_D^{20} 1.4422, d_4^{20} 0.7297, MR_D 34.86. C_7H_{12} . Calc. 33.57; EMR_D 1.29.

0.2276 g sub.: 0.7335 g CO_2 ; 0.2571 g H_2O . 0.1534 g sub.; 26.16 g benzene Δt 0.34°. Found %: C 87.88; H 12.64. M 94.5. C_7H_{12} . Calculated %: C 87.41; H 12.59. M 96.

Literature data for heptadiene-1,3: b.p. 100.55° (747.6 mm), d_4^{20} 0.7222, n_D^{20} 1.4428 [23].

Hydrogenation of the 103-103.6° fraction. 0.5937 g of the hydrocarbon in alcohol solution with 0.1 g of platinum black was hydrogenated by 251 ml of hydrogen (NTP). Found: diethylenic hydrocarbons 81.2%, ethylenic 18.8%.

The saturated hydrocarbon formed by the hydrogenation of 3.9 g of the 103-103.6° fraction, was washed free from alcohol by saturated common salt solution, dried by calcium chloride, and distilled over sodium. The main mass distilled at 98.2°.

d_4^{20} 0.6877, n_D^{20} 1.3887.

0.1836 g sub.: 0.5679 g CO_2 ; 0.2644 g H_2O . 0.1145 g sub.; 19.26 g benzene: Δt 0.325°. Found %: C 84.35; H 16.13, M 99.1. C_7H_{16} . Calculated %: C 83.89; H 16.11, M 100.2.

Literature data for n-heptane: b.p. 98.4°, d_4^{20} 0.6837, n_D^{20} 1.3877 [24].

The hydrogenation product of the 103-103.6° fraction was normal heptane, and therefore the original unsaturated hydrocarbon had a normal carbon chain.

Action of sulfur dioxide solution on the 103-103.6° fraction. By the action of aqueous sulfur dioxide solution on a sample of the fraction, a white cake of amorphous polymer sulfone was formed (characteristic for hydrocarbons with conjugate double bond systems).

Ozonation of the 103-103.6° fraction. 2 g of the freshly distilled hydrocarbon in chloroform solution was ozonized by Yakubchik's method [25], developed for the determination of vinyl groups in rubbers. After removal of chloroform from the ozonides under vacuum, water was added to the residue heated to 25°, and the mixture was heated 3 hours on the water bath to decompose the ozonides. Formaldehyde was determined quantitatively in the ozonolysis products by means of the reaction product with β -naphthol [26], and formic acid was determined from the calomel precipitate formed by heating the sample with mercuric chloride solution [27]. By these determinations it was possible to determine the content of the $CH_2=C<$ end group in the hydrocarbons studied and to indicate the amount of diethylenic hydrocarbon with a conjugate system in the 1,3 position.

Found: formaldehyde 0.2%, formic acid 80.4%, calculated on C_7H_{12} .

The results show that the substance investigated contained 80.6% of a hydrocarbon with a double bond at the end of the chain, and therefore, with a conjugate system in the 1,3 position. The diethylenic hydrocarbon content determined by hydrogenation (81.2%) was close to the results found by ozonolysis. The remainder was probably the C_7 ethylenic hydrocarbon with the double bond in the middle of the chain, the formation of which may be assumed in this process (for example, in the Lebedev reaction some pseudobutylene is formed from ethyl alcohol, in addition to divinyl [1]).

Condensation of the 103-103.6° fraction with maleic anhydride. 0.8 g of maleic anhydride in benzene solution was added to 0.85 g of the fraction freshly distilled over sodium. The mixture was left to stand for 24 hours and the benzene was distilled off by warming in vacuum. The reaction product was washed with cold water. Water was removed from the remaining oil by heating to 90° in vacuum. Pale yellow crystals separated on cooling. After 3-fold recrystallization from benzene they melted at 50°.

0.0714 g sub.; 25.38 g benzene: Δt 0.08°. Found: M 192.9. $C_{11}H_{14}O_3$. Calculated: M 194.

Investigation of the 109.2-109.7° fraction

By its boiling point this fraction corresponded to heptadiene-2,4:

d_4^{20} 0.7386, n_D^{20} 1.4582, MR_D 35.44, C_7H_{12} . Calc. 33.57; EMR_D 1.87.

0.2130 g sub.: 0.6835 g CO_2 ; 0.2372 g H_2O . 0.1911 g sub.: 27.30 g benzene: Δt 0.303°. Found%: C 87.51; H 12.46. M 94.6. C_7H_{12} . Calculated %: C 87.41; H 12.59. M 96.

Literature data for heptadiene-2,4 [28]: b.p. 109.6°, d_4^{20} 0.7384, n_D^{20} 1.4578.

An amorphous white cake of polymer sulfone was formed by the action of aqueous sulfur dioxide solution on the 109.2-109.7° fraction.

The condensation product of the 109.2-109.7° fraction with maleic anhydride in benzene solution (after removal of benzene, washing with water to remove unreacted maleic anhydride, and 4-fold recrystallization) melted at 69.5°; according to the literature the melting point of the maleic anhydride adduct with heptadiene-2,4 is 70.5° [28].

Investigation of the Raman spectra of the 103-103.6° and 109.2-109.7° fractions

The combinational light scattering (Raman) spectra were studied by means of visual estimation of intensity.

Spectral analysis data for the 103-103.6° fraction (in cm^{-1}): 1106 (3), 1163 (4), 1181 (3), 1300 (3), 1374 (3), 1449 (2), 1609 (3), 1655 (10).

The 1609 and 1655 frequencies and their high intensities indicate the presence of a conjugate double bond system. Owing to lack of literature data on the spectrum of heptadiene-1,3 we compared our results with the spectral frequencies for pentadiene-1,3. Slobodin and Shokhor [29], and Slobodin and Khokhlacheva [30] found the frequencies 1569, 1603, 1646, 1655, for pentadiene-1,3, which probably correspond to the cis form (1596 and 1646) and the trans form (1603 and 1655). Apparently the fraction investigated by us contains heptadiene with a conjugate system in the 1,3 position, corresponding to the trans form (1609 and 1655).

Spectral analysis data for the 109.2-109.7° fraction (in cm^{-1}): 850 (3), 889 (2), 962 (1), 1010 (2), 1058 (2), 1086 (5), 1115 (6), 1149 (8), 1172 (10), 1201 (5), 1253 (8), 1276 (4), 1300 (6), 1308 (5), 1449 (6), 1512 (1), 1563 (3), 1600 (4), 1659 (20), 1664 (20).

The frequencies 1659 and 1664 and their high intensities indicate the presence of a conjugate double bond system. A comparison of these frequencies with the frequencies 1654 and 1663 in the spectrum of heptadiene-2,4, determined by Treshcheva, Tatevsky, Levina, and others [31], and also with the frequencies 1656 and 1668 in the spectrum of hexadiene-2,4, obtained by Tatevsky, Treshcheva, Skvarchenko, and Levina [32] leads to the conclusion that the heptadiene studied has a conjugate double bond system in the 2,4 position.

Investigation of the other hydrocarbon fractions

The fractions corresponding to the C_6 hydrocarbons were collected by means of the distillation column in the ranges 77-77.5° and 77.5-78°. Their d_4 , n , and MR were determined, and also the diethylenic hydrocarbon content by hydrogenation over platinum. It was shown that these fractions contained a mixture of ethylenic and diethylenic C_6 hydrocarbons, formed by conversion of acetone in the given conditions [16].

The 132-133° fraction by the results of d , n , and MR determinations and from the hydrogenation results, corresponds to a mixture of C_8H_{14} and C_8H_{16} hydrocarbons, the conversion products of *n*-butyl alcohol over Lebedev's catalyst. These hydrocarbons were studied by us previously [17], and therefore they were not investigated in greater detail.

We express our gratitude to Ya. M. Slobodin for assistance in investigation of the Raman spectra.

SUMMARY

1. The conversion of a mixture of *n*-butyl alcohol with acetone into C_7H_{12} hydrocarbons with conjugate double bond systems over mixed Lebedev's catalyst has been studied.

2. It was established that the hydrocarbons formed have a normal carbon chain, and are heptadiene-1,3 and heptadiene-2,4. These hydrocarbons are formed in a 2:1 ratio.

3. The reaction products also contain butyraldehyde, isopropyl alcohol, butylene, propylene, and also C_6 hydrocarbons (by acetone conversion) and C_8 hydrocarbons (by butyl alcohol conversion).

4. A scheme is put forward for the catalytic conversion of a mixture of n-butyl alcohol with acetone into diethylenic C_7H_{12} hydrocarbons, based on the concept of mixed condensation of butyraldehyde with acetone to give butylideneacetone, followed by its reduction by butyl alcohol to an unsaturated alcohol, and dehydration of the latter to form the isomeric heptadienes (1, 3 and 2, 4).

5. An explanation is given for the formation of heptadiene as a by-product in the catalytic conversion of ethyl alcohol into divinyl by Lebedev's method.

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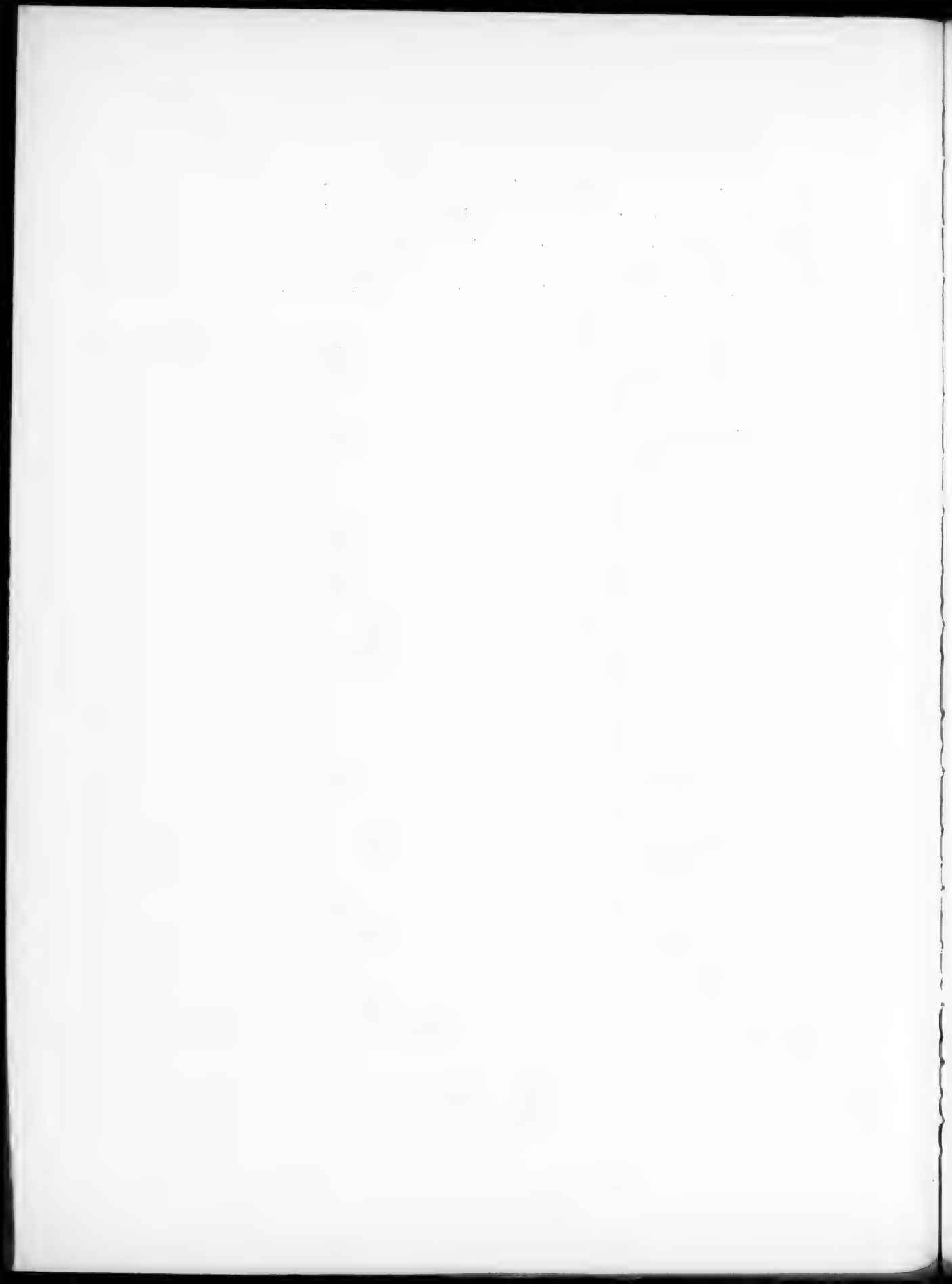
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THE HYDROGENATION RATE OF AROMATIC HYDROCARBONS

VIII. HYDROGENATION OF CONDENSED AROMATIC HYDROCARBONS IN THE PRESENCE OF TUNGSTEN DISULFIDE

A. V. Lozovoi and S. A. Senyavin

In the previous communication[1] we described the results of measuring the relative hydrogenation rates of benzene and a number of its homologs under high hydrogen pressure, at elevated temperature, and in the presence of WS_2 as catalyst. Then we studied the hydrogenation rates of the condensed aromatic hydrocarbons and their hydro derivatives. These compounds are found in the products obtained from the liquid phase hydrogenation of coal and primary tars, and are also contained in appreciable amounts in petroleum and the products of its refining. As is known, in the second, the so-called vapor phase step in the destructive hydrogenation of fuel oil, carried out in the presence of WS_2 as catalyst, the material subjected to hydrogenation is the oil fraction, containing the indicated hydrocarbons, obtained in the first, liquid phase stage of the process.

While some data for the relative hydrogenation rates of the simpler condensed aromatic hydrocarbons — naphthalene, anthracene, phenanthrene, acenaphthene — in the presence of $Ni + Al_2O_3$ and MoS_2 catalysts exist in the literature [2,3,4], analogous information for their hydrogenation over WS_2 is available in neither the Soviet nor the foreign literature. In the meantime, a study of the hydrogenation kinetics of condensed aromatic hydrocarbons in the presence of WS_2 is of essential interest, since it is the basic catalyst in the vapor phase steps of the commercial process for the destructive hydrogenation of fuel oil.

In the present communication are given the results of determining the relative hydrogenation rates at 400° , a pressure of 150 atm, in the presence of WS_2 , of naphthalene into tetralin, anthracene into di-, tetra- and octahydroanthracenes, and also of chrysene into some of its hydro derivatives, in comparison to the hydrogenation rate of benzene.

Method of Study and its Objectives

The method of measuring the hydrogenation rates of condensed aromatic hydrocarbons in principle was the same as that described in previous communications [1,7]. Calculation of the amount of hydrogenated hydrocarbon was essentially based on the method of measuring the amount of reacted hydrogen. To the rotated hydrogenation autoclave, having a volume of 0.6 liters, was connected a 0.125 liter calibrated high pressure hydrogen bomb. As the hydrogen was used up in the autoclave and the pressure fell the needed amount of hydrogen was added from the bomb, measured by the reading of the control manometer (with a scale division of 2 atm) on the bomb. The used method assured measurement of the degree of hydrogenation to an accuracy of not less than $\pm 1\%$, and in most of the experiments the accuracy was greater than this.

The characteristics of the hydrocarbons used in the experiments are given in Table 1.

A fresh portion of the WS_2 catalyst, described in the previous communication [1], was used in each experiment, in an amount ranging from 1.5 to 40% on the weight of hydrocarbon being hydrogenated. Electrolytic hydrogen was used in the hydrogenations.

The degree of hydrocarbon hydrogenation toward the end of the experiment failed to exceed 80%. The experiment was prolonged for 60 to 90 minutes, in which connection the reaction rate was measured every 5 to 30 minutes.

At the beginning of hydrocarbon hydrogenation the reaction rate dropped somewhat, but it quickly stabilized and during the period of making measurement it remained constant or dropped slowly in the majority of cases. The decrease in the hydrogenation rate at the beginning of the experiment was apparently due to the reduction of the WS_3 , present in the catalyst and possessing a higher activity than the less active but more stable WS_2 .

The reaction rate was expressed in moles of hydrocarbon reacted in one minute. Inasmuch as the reaction rate during the time of measurement was practically constant, the molar amount of hydrocarbon, hydrogenated per unit of

TABLE I

Exp. No.	Hydrocarbons	Melting point	Boiling point	n_D^{20}	Method of Preparation
1	Benzene	—	79.75–80.0° (761 mm)	1.5000	—
2	Tetralin	—	205–207 (758 mm)	1.5411	—
3	Naphthalene	80.5°	—	—	Purified with 5% Na at 120–130°
4	Anthracene	214–215	—	—	—
5	9,10-Dihydroanthracene	103–110	—	—	Anthracene hydrogenated to the addition of 1 mole of H_2 per mole of compound in the presence of WS_2 at 400° and 150 atm.
6	Tetrahydroanthracene, white crystals	—	—	—	9,10-Dihydroanthracene hydrogenated under the above indicated conditions with the addition of 1 mole of H_2 per mole of compound
7	Octahydroanthracene, white crystals, probably a mixture of symmetrical and unsymmetrical octahydroanthracene*	Crystallizes on standing	290–295	1.5588	Tetrahydroanthracene hydrogenated under the same conditions to the addition of $2H_2$ per mole of compound. Elementary composition: C-90.18%, H-9.82%; calculated for $C_{14}H_{18}$: C-90.22%, H-9.78%.
8	Chrysene, yellow crystals	249–252°	—	—	—
9	Tetrahydrochrysene (structure not established), light yellow crystals	128–136	—	—	Chrysene hydrogenated under the above indicated conditions to the addition of $2H_2$ per mole of compound
10	Octahydrochrysene, a mixture of isomers	—	290–380: 300–154%, 300–320, 192%, 320–340, 192%, 340–370, 27%	1.5660	Tetrahydrochrysene hydrogenated under the above indicated conditions to the addition of $2H_2$ per mole of compound

* The simultaneous formation of the symmetrical and unsymmetrical octahydroanthracene in the hydrogenation of tetrahydroanthracene in the presence of MoS_2 was shown by Prokopets and coworkers [4]. The hydrogenation in the presence of WS_2 probably proceeds in a similar manner. According to the literature [5], the boiling point of the symmetrical octahydroanthracene is 293–295°, of the unsymmetrical it is 292–295°.

time, served as a direct expression of the reaction rate constant for the hydrogenation of the investigated hydrocarbon. The ratio of the latter to the rate constant for the hydrogenation of benzene, taken as 100 (or tetralin as 250) [1], expressed the relative hydrogenation rate of condensed aromatic hydrocarbons and their partially hydrogenated products.

In the gases, remaining in the autoclave after measuring the hydrogenation rates for the hydrogenated derivatives of anthracene and chrysene, we failed to detect the presence of any methane hydrocarbons, with the exception of the hydrogenation of octahydrochrysene, where in the gas after hydrogenation there was found 2% of C_nH_{2n+2} hydrocarbons. This indicates incipient destruction of the hydrogenated chrysene derivatives, as a result of which the hydrogenation of chrysene was terminated at the dodecahydrochrysene stage, after 65% of the theoretical amount of hydrogen had been absorbed.

DISCUSSION OF RESULTS

In Table 2 are given the experimental data on the hydrogenation rate of naphthalene into tetralin into decalin, and of anthracene and three of its hydro derivatives in comparison to the naphthalene hydrogenation rate; in Table 3, the rates for the hydrogenation of chrysene and its hydro derivatives are compared with the hydrogenation rate for ben-

zene. In Table 4 are given the summarized measurement results for the relative hydrogenation rates of nine studied hydrocarbons, in which connection in some of the cases the hydrogenation rate is compared with the corresponding values obtained for hydrogenation in the presence of MoS_2 [7] and $\text{Ni} + \text{Al}_2\text{O}_3$ [2].

As can be seen from the data in Table 4, the hydrogenation kinetics for condensed aromatic hydrocarbons is characterized by complexity and specificity. For the simpler members of these hydrocarbons — naphthalene, anthracene, and also acenaphthene and phenanthrene (their hydrogenation rate was studied in the presence of $\text{Ni} + \text{Al}_2\text{O}_3$ [2]) it is characteristic for the reaction to proceed in stepwise fashion through successive hydrogenation stages — into the di-, tetra-, octa- and perhydro derivatives. The first hydrogenation stages in the presence of all of the hydrogenation catalysts studied by us proceed with considerable rapidity, being ten times as great as the hydrogenation rate in the last stages, when the benzene ring is saturated.

On passing to a more complex aromatic hydrocarbon, namely chrysene, the kinetics of high temperature hydrogenation in the presence of WS_2 changes: the hydrogenation loses its stepwise nature with an extremely high initial and gradually decreasing (in measure with the degree of hydrogenation) rate, and from the very beginning the reaction proceeds slowly at a constant rate, somewhat slower than the hydrogenation rate of benzene and 30-80 times slower than the hydrogenation rates of naphthalene and anthracene. The practically constant hydrogenation rate of chrysene was retained up to 65% of the theoretical amount of hydrogen absorption. The structure of chrysene (I) predicates the possibility of either the successive or the simultaneous hydrogenation of synonymous rings 1 and 4. Judging from the

TABLE 2
Relative Hydrogenation Rates of Naphthalene, Anthracene and Their Hydro Derivatives
Temperature 400°, Pressure 150 Atm., Catalyst WS_2

Exp. No.	Hydrocarbon and Studied Reaction	Amount of Catalyst (in Wt. %)	Duration of Experiment (in Min.)	Amount of Hydrogenated Hydrocarbon (in Moles)	$K_0 \cdot 10^4 \frac{\text{mole}}{\text{min}} \cdot 10^4$	Relative Hydrogenation Rate (Hydrogenation Rate of Benzene 100)
1	Naphthalene, 40 g, hydrogenation to tetralin	10.0	60	0.249	41.5	2300*
2	Tetralin, 40 g, hydrogenation to decalin	10.0	60	0.027	4.5	250**
3	Naphthalene, 40 g, hydrogenation to tetralin	1.5	84	0.133	15.8	2300
4	Anthracene, 40 g, hydrogenation to dihydroanthracene	1.5	44	0.187	42.5	6187
5	Naphthalene, 34 g, hydrogenation to tetralin	1.5	84	0.113	13.5	2300
6	9, 10-Dihydroanthracene, 32.8 g and 34.9 g, hydrogenation to tetrahydroanthracene	1.5	90	0.068	7.6	1295
7						
8	Naphthalene, 31.2 g, hydrogenation to tetralin	10.0	60	0.194	32.3	2300
9	Tetrahydroanthracene, 31.2 g, hydrogenation to octahydroanthracene	10.0	60	0.0379	6.3	449
10	Naphthalene, 17 g, hydrogenation to tetralin	10.0	60	0.0993	16.6	2300
11						
12	Octahydroanthracene, 17 g, hydrogenation to perhydroanthracene	10.0	60	0.01264	2.1	291
13						

constancy of the rate for the addition of the first eight hydrogen atoms, it is more probable to assume the simultaneous hydrogenation of these two rings with the direct formation of octahydrochrysene. The transition to the hydrogenation of the octahydrochrysene is accompanied by a certain change in the reaction rate. But since the structure of the equivalent rings 2 and 3 in octahydrochrysene fails to differ in principle from the structure of rings 1 and 4 in the chrysene molecule, then a considerable change in the reaction rate is not observed, such as is revealed in the transition from the initial to the last stages in the hydrogenation of naphthalene and anthracene. Also, there is no basis to expect a reduction in the reaction rate on further hydrogenation, in the presence of

* Calculated from the hydrogenation rate of tetralin.

** [1].



TABLE 3

Relative Hydrogenation Rates of Chrysene and Its Hydro Derivatives in the Presence of WS_2 (40%)
Temperature 400°, Pressure 150 Atm., Duration of Experiments 60 Minutes

Exp. No.	Hydrocarbon and Studied Reaction	Amount of Hydrocarbon Hydrogenated in the Exp. Time (in Moles)	$K_0 \cdot 10^4$ $\left(\frac{\text{mole}}{\text{min}} \cdot 10^4\right)$	Relative Hydrogenation Rate
14	Benzene, 30 g	0.0576	9.6	Taken equal to 100
15	Chrysene, 30 g, hydrogenation to tetrahydrochrysene	0.0460	7.67	80
16	Tetrahydrochrysene, 30 g, hydrogenation to octahydrochrysene	0.0440	7.33	76
17	Benzene, 20 g	0.0382	6.37	100
18	Octahydrochrysene, 10.8 g, hydrogenation to dodecahydrochrysene	0.0367	6.12	96

TABLE 4

Relative Hydrogenation Rates of Condensed Aromatic Hydrocarbons and Their Hydro Derivatives

Exp. No.	Hydrogenation Reaction	Relative Rate With the Hydrogenation Rate of Benzene Taken Equal to 100		
		Catalysts and Hydrogenation Conditions		
		WS_2 , 400°, 150 atm	MoS_2 , 420° [7] 200 atm	$Ni + Al_2O_3$ [2] 120-202°, 30-50 atm
1	Naphthalene → tetralin	2300	1409	314
2	Tetralin → decalin	250	287	24
3	Anthracene → 9,10-dihydroanthracene	6187	—	326
4	9,10-Dihydroanthracene → tetrahydroanthracene	1295	—	308
5	Tetrahydroanthracene → octahydroanthracene	449	—	147
6	Octahydroanthracene → perhydroanthracene	291	—	4
7	Chrysene → tetrahydrochrysene	80	—	—
8	Tetrahydrochrysene → octahydrochrysene	76	—	—
9	Octahydrochrysene → dodecahydrochrysene	96	—	—

WS_2 , of the formed dodecahydrochrysene, since the hydrogenation of the last benzene ring should proceed at a rate close to the hydrogenation rate of benzene [1].

Judging from the complexity of the chrysene hydrogenation products, being a multicomponent mixture, together with the described basic reaction course, it is also possible to have the simultaneous addition of hydrogen in two other directions, in particular the successive hydrogenation of rings 1 and 4, 1 and 2 and the simultaneous hydrogenation of rings 1 and 2. The probability of such reaction courses is demonstrated by the studies of Prokopets, Pavlenko and Boguslavskaya on the mechanism for the hydrogenation of tetrahydroanthracene [4] and also by the studies of Coulson [6]. The latter, who hydrogenated pyrene in the presence of $MoOS$, obtained a mixture of hydro derivatives ranging from the di- to the decahydropyrene.

If, on the one hand, the relative hydrogenation rates of naphthalene (2300) and its derivatives — tetrahydroanthracene (449) and octahydrochrysene (96) — are compared, with the hydrogenation rates of benzene (100) and its derivatives — tetralin (250) and octahydroanthracene (291) — on the other hand, then it can easily be seen that an essential difference exists in the nature of the influence exerted by increasing the complexity of the molecule structure on the hydrogenation rate in the presence of WS_2 for the two classes of aromatic hydrocarbons — condensed and noncondensed: for the first the hydrogenation rate drops sharply with increase in molecule size (the chemical character of the condensed aromatic rings remaining constant); for the second, saturating the benzene ring, the hydrogenation rate not only fails to decrease in measure with increase in the molecular weight of the compound (due to the accumulation

of side saturated rings and chains), but it noticeably, and in some cases [1], strongly rises.

The influence of increased molecule complexity on the hydrogenation rate of condensed aromatic hydrocarbons is brought out very clearly on comparing the hydrogenation rates of naphthalene and chrysene. The latter, not differing from naphthalene in the character of its structure and, consequently, in the degree of unsaturation, is hydrogenated at a rate nearly 30 times slower than naphthalene.

Apparently, this is explained by the fact that the larger unsaturated molecules, first, simultaneously react with a large number of active catalyst centers and consequently the catalyst efficiency diminishes, and second, and this may have decisive significance, the higher molecular weight hydrogenation products are desorbed with greater difficulty from the catalyst surface, which also reduces its efficiency. Here, apparently, it is necessary to seek a reason for the fact that with a certain degree of molecule complexity the hydrogenation rate of the aromatic condensed hydrocarbon becomes even less than the hydrogenation rate of benzene.

Different relationships are observed in the hydrogenation (in the presence of WS_2) of benzene and its derivatives: an increase in the size of the aromatic hydrocarbon molecule due to saturated condensed cycles (order: benzene \rightarrow tetralin \rightarrow octahydroanthracene) or alkyl radicals [1] causes an increase in the hydrogenation rate. In order to explain these seemingly contradictory relationships it is necessary to take into consideration that: 1) condensed aromatic hydrocarbons from the nature of their unsaturated bonds are capable of adding hydrogen at a considerably faster rate than is the benzene ring; 2) for the catalytic addition of hydrogen to any unsaturated compound it is necessary for the latter to be in contact with the active catalyst centers for a definite length of time in the chemically sorbed state. The more difficult the compound is to hydrogenate, the longer, apparently, should be the time required for the chemisorption reaction. For rapidly reacting condensed aromatic hydrocarbons a prolonged chemisorption of the molecule being hydrogenated on the active catalyst centers and a slow desorption of the hydrogenation products retards the reaction course. The factors, causing the prolonged existence of the reacting substances and reaction products on the catalyzing surface, such as the strong adsorption and slow desorption conditioned by increasing molecule complexity, should favor a drop in the hydrogenation rate (in the case of chrysene and tetrahydroanthracene).

For single ring aromatic hydrocarbons that hydrogenate slowly it is necessary to have a longer chemisorption period on the catalyst. The great tendency of the molecule to be adsorbed on the catalyst surface, usually increasing with increase in molecule complexity, can create, in the case of difficultly hydrogenated compounds, more favorable conditions for reaction and, in the final analysis, can accelerate the reaction, especially if the hydrogenation products are quickly removed from the catalyst surface. For example, the duration of the benzene molecule in the adsorbed condition on the surface of a catalyst with relatively low activity may prove to be insufficient for hydrogenation. Increasing the complexity of the benzene molecule by introducing alkyl substituents or a saturated condensed cycle into the ring increases absorption of the aromatic hydrocarbon on the catalyst and in this way, under the same reaction conditions, creates more favorable possibilities for reaction of the aromatic hydrocarbon with hydrogen. However, in the case of hydrogenation in the presence of a highly active catalyst, the indicated increase in the complexity of the benzene molecule may not cause accelerated hydrogenation of the aromatic ring, since in this case a prolonged existence of the hydrocarbon molecule in the chemically sorbed state on the active centers of the catalyst is not necessary for achieving the addition of hydrogen to the benzene ring. Apparently, a similar phenomenon is also observed in the case of hydrogenating single ring aromatic hydrocarbons in the presence of the highly active catalyst MoS_2 at elevated temperature: benzene, toluene, m-xylene and pentamethylbenzene all add hydrogen at practically the same rate at 420° [7].

On lowering the hydrogenation temperature in the presence of highly active catalysts an increase in the complexity of the aromatic hydrocarbon can, in certain cases, create difficulties for bringing up the activated hydrogen atoms to the molecule being hydrogenated on the catalyst surface. A similar phenomenon was observed [8] in the hydrogenation of benzene and its methyl derivatives in the presence of $Ni + Al_2O_3$ at $120-200^\circ$. In the case of hydrogenation in the presence of MoS_2 at 240° it was also revealed that m-xylene adds hydrogen at a rate 1.3 times slower than benzene, while at elevated temperature (420°) the hydrogenation rates for benzene and m-xylene are the same.

From the practical viewpoint it is essential to mention that in the hydrogenation of fuel crudes, containing condensed aromatic hydrocarbons, in the presence of WS_2 and similar high temperature catalysts, a reduction in the hydrogenation rate should be observed in measure with increase in the degree of hydrogenation and with increase in the boiling point (molecular weight) of the fractions being hydrogenated.

SUMMARY

The relative hydrogenation rates of the condensed aromatic hydrocarbons — naphthalene, anthracene, chrysene and their hydro derivatives — were measured in the presence of WS_2 catalyst, at 400° , and a pressure of 150 atm.

It was found that with the hydrogenation rate for benzene taken as 100, that the hydrogenation rates (in round numbers) are: naphthalene - 2300, anthracene - 6200, 9,10-dihydroanthracene - 1300, tetrahydroanthracene - 450, octahydroanthracene - 290, chrysene - 80, and octahydrochrysene - 96.

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SULFONATION REACTION

XXXIV. Hydrolysis of Sulfonic Acids of the Benzene Series

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It is known that the sulfonic acid mixtures, formed in the low temperature sulfonations of toluene or phenol, contain a large amount of the *o*-sulfonic acid, which on elevating the temperature is converted in the reaction mixture into the *para*- isomer, due to the fact that the *ortho*- isomer is more easily hydrolyzed than the *para*- isomer. Hydrolysis of the unstable *ortho*- isomer and repeated sulfonation lead to a mixture rich in the *para*- isomer. Experiments on the hydrolysis of the sulfonic acid isomers of the benzene series were made by Obermiller [1], who heated the sodium salts of *o*-, *p*- and *m*-phenolsulfonic acids with excess hydrochloric acid on the water bath for 7 and 9 hours. These experiments revealed that the *meta*- isomer is completely resistant to hydrolysis, the *para*- isomer is hydrolyzed to the extent of 31-37 %, while the *ortho*- isomer is 97-99% hydrolyzed.

Vesely and Stojanova [2] in determining the hydrolysis temperatures of different sulfonic acids found that *m*-toluene-sulfonic acid begins to hydrolyze at 155°, the *p*- acid at 186°, and the *o*- acid at 188°. As a result, of the three isomers the *meta*- isomer is most easily hydrolyzed and the *ortho*- isomer is the most difficult. *m*-Chlorobenzenesulfonic acid also begins to hydrolyze before (182°) its *para*- isomer (200°).

Consequently, according to the data of Obermiller, the kinetic stability of hydrolysis of the isomeric phenol-sulfonic acids follows the order: $m > p > o$, and according to the data of Vesely and Stojanova, the stability to hydrolysis of the isomeric toluenesulfonic acids is in the order: $o > p > m$.

In the present paper we studied the influence of the position of different substituents in the benzene ring on the hydrolysis rate of sulfonic acids, the isomerization of the *para*- isomer of phenolsulfonic acids, and the hydrolysis of benzenepolysulfonic acids.

EXPERIMENTAL

For the study benzenesulfonic acids were chosen, containing the ring activation group I of type ($-OH$), the ring deactivation group I of type ($-Cl$), group II of type ($-COOH$) and the amino group, changing orientation in strongly acid medium.

To a weighed sample of the sulfonic acid in a test tube was added either hydrochloric or phosphoric acid in such amount and such concentration as would give about 4.5 moles of water per mole of sulfonic acid. The stoppered test tube was kept at a definite temperature, and then, after dissolving the mixture in water, the amount of hydrolyzed sulfonic acid was found from the amount of formed sulfuric acid, which was determined gravimetrically as barium sulfate.

The experimental results, given in Table 1, show that with any of the investigated substituents the kinetic stability to hydrolysis of isomeric sulfonic acids follows the order: $m > p > o$. Only in the case of the *p*- and *m*-sulfobenzoic acids were we unable to achieve a definite result.

And so the experiments revealed that *m*-phenolsulfonic acid is considerably more stable than the *para*- isomer. With the purpose of initiating experiments on the isomerization of these acids we determined at which temperatures noticeable hydrolysis of the *para*- isomer begins. In the literature Armstrong and Miller [3] have reported on the hydrolysis of the *para*- isomer. They mentioned a temperature of 116° as denoting the beginning of hydrolysis for the acid. Later Bruckner [4] indicated that 123-125° was the hydrolysis temperature for *p*-phenolsulfonic acid. Our hydrolysis was carried out without mineral acid. The experimental results, given in Table 2, reveal that the *para*- isomer is noticeably hydrolyzed below 80°. Apparently, the mentioned authors indicated slightly high temperatures, due to the fact that they studied the hydrolysis in the presence of a large amount of water. Despite the fact that Experiments 276, 332 and 335 (Tables 1 and 2) were carried out under different conditions (at different temperatures, with hydrochloric acid or without it), almost the same result was obtained in all three cases — about 44% of the *p*-phenolsulfonic acid was hydrolyzed. This is explained as being due to the formation of evolved sulfuric acid in the reverse of the phenol sulfonation reaction, the concentration of which in Experiment 276 attains a value of 36.5 %.

TABLE 1

Exp. No.	Sulfonic Acid	Moles of water taken per mole of sulfonic acid	Mineral acid		Temperature	Time (in hours)	Amount of hydrolyzed sulfonic acid (in %)
			Nature	Concentration in the mixture (in %)			
332	p-Phenol-	4.68	HCl	16.9	101°	25	45.7
335	p-Phenol-	4.45	HCl	18.1	109.5	25	44.1
334	m-Phenol-	4.58	HCl	18.5	109.5	25	0.4
336	m-Phenol-	4.53	HCl	16.8	126	25	1.1
324	o-Chlorobenzene-	4.47	H ₃ PO ₄	79.6	163	100	49.1
326	p-Chlorobenzene-	4.59	H ₃ PO ₄	79.5	163	100	14.4
325	m-Chlorobenzene-	4.74	H ₃ PO ₄	78.5	163	100	2.2
321	o-Chlorobenzene-	4.58	H ₃ PO ₄	79.8	184	8	30.0
323	p-Chlorobenzene-	4.63	H ₃ PO ₄	79.4	184	8	7.7
322	m-Chlorobenzene-	4.74	H ₃ PO ₄	79.3	184	8	1.9
315	o-Sulfobenzoic	4.49	H ₃ PO ₄	52.9	185	12	7.6
314	p-Sulfobenzoic	4.51	H ₃ PO ₄	55.5	185	12	0
316	m-Sulfobenzoic	4.51	H ₃ PO ₄	55.3	185	12	0
308	Orthanilic	4.48	H ₃ PO ₄	61.6	184	4	89.6
307	Sulfanilic	4.55	H ₃ PO ₄	62.4	184	4	2.2
309	Metanilic	4.49	H ₃ PO ₄	61.8	184	4	0
305	Orthanilic	4.50	H ₃ PO ₄	61.6	211	4	89.8
304	Sulfanilic	4.50	H ₃ PO ₄	62.4	211	4	66.2
306	Metanilic	4.51	H ₃ PO ₄	61.8	211	4	0

TABLE 2

Hydrolysis of p-Phenolsulfonic Acid

Exp. No.	Moles of Water taken per mole of sulfonic acid	Temperature	Time (in hours)	Hydrolyzed (in %)
276	4.55	100°	25	43.5
280	4.34	79	25	3.5
277	4.47	66	25	0

TABLE 3

Action of Sulfuric Acid on Benzoic Acid for 8 Hours at 163°

Exp. No.	Sulfuric Acid concentration	Amount of reacted sulfuric acid (in % of amount taken)
285	99.6	17.4
289	94.7	13.5
291	88.6	3.4

TABLE 4

Hydrolysis of Benzene Di- and Trisulfonic Acids

Exp. No.	Sulfonic Acid	H ₂ SO ₄ concentration in the mixture	Moles of water per mole of sulfonic acid	Temperature	Time (in hours)	Hydrolyzed (in %)
273	1,3-Benzenedi-	84.5	2.1	234°	8	11.8
272	1,3,5-Benzendi-	0	4.0	235	8	0
274	1,3,5-Benzenetri-	85.3	2.0	234	8	0
287	1,3,5-Benzenetri-	83.7	2.1	285	8	Oxidation

The following experiment revealed that even a lower concentration of sulfuric acid in the sulfonation mixture can sulfonate phenol. One gram of phenol and 1 g of 70% sulfuric acid was heated at 101.5° for 48 hours. Titration of the sulfonation mixture, dissolved in water, with 0.1 N alkali solution revealed that the concentration of sulfuric acid in the reaction product had dropped to 32%.

As a result, in three experiments on the hydrolysis of p-phenolsulfonic acid fairly rapid equilibrium is reached between phenol and the sulfonic acid on the one hand, and between the sulfonic acid and water on the other hand. However, this is a false equilibrium, for at the same time the process for the transformation of the less stable para-

isomer into the more stable meta- isomer is taking place. The transformation of the para- isomer into the meta- isomer proceeds very slowly at 100°.

We attempted to isomerize the p-phenolsulfonic acid in the presence of sulfuric acid at 163°. For this it was necessary to know the sulfuric acid concentration at which neither appreciable disulfonation occurs, nor the significant formation of phenol due to hydrolysis. In two experiments weighed samples of p-phenolsulfonic acid were heated at 163° for 8 and 25 hours with 62.8% (2.4 moles) and with 58.8% (2 moles) sulfuric acid. Titration with alkali revealed that in the first experiment the sulfuric acid concentration dropped to 61.6%, i.e., a slow disulfonation was taking place, while in the second experiment there was hardly any change (59.0%).

Making use of the obtained data, two experiments on the isomerization of p-phenolsulfonic acid were made in the following manner. A weighed sample of the p- acid was heated with 2.06 moles of 59.4% sulfuric acid per mole of sulfonic acid at 163° for 25 hours in a sealed tube. After dissolving in water, the mixture was analyzed by the method of gravimetrically determining the amount of sulfuric acid before and after bromination of part of the solution with bromide-bromate. Since in the bromination the sulfonic group is displaced from the para- isomer and not from the meta- isomer, then by difference, obtained by subtracting the sulfuric acid, found after and before bromination, the amount of meta- isomer in the mixture was determined, in the first experiment being equal to 12.8% of the total amount of phenolsulfonic acids.

In the second experiment 2.09 moles of 60% sulfuric acid per mole of sulfonic acid was taken. Heating at 163° was continued for 150 hours. In the water solution there separated a black insoluble deposit, representing 3.7% of the sulfonic acid weight, and consequently it was filtered off before analysis. This introduced some error in the analysis result, which showed a m-phenolsulfonic acid content of 39.3%.

These experiments revealed that there exists not only transformation of o-phenolsulfonic acid into the para- isomer on raising the temperature, but also that the latter is transformed, to be sure, much more slowly into the m-sulfonic acid, being the isomer most stable to hydrolysis.

The experiments further revealed (Table 1) that the sulfobenzoic acids are extremely stable to hydrolysis. Since sulfuric acid [5] facilitates the hydrolysis, experiments were set up in its presence. A preliminary study of the action of sulfuric acid on benzoic acid revealed (Table 3) that 88% sulfuric acid at 163° still sulfonates benzoic acid; consequently, to exclude the sulfonation process, all three of the sulfobenzoic acid isomers were heated with 70% sulfuric acid for 12 and 75 hours at 163°. However, not one of the isomers suffered hydrolysis. The p-sulfobenzoic acid also fails to be appreciably hydrolyzed at 233° for 4 hours with 82% phosphoric acid.

The sulfonic acids of aniline hydrolyze with greater ease, as is shown by the experimental results presented in Table 1. Only the metanilic acid failed to be hydrolyzed, while the orthanilic acid is hydrolyzed even at 163° (25% in 12 hours).

Finally, the benzenedi- and trisulfonic acids were subjected to hydrolysis. The experimental results, presented in Table 4, reveal that benzenetrisulfonic acid fails to lend itself to hydrolysis. On opening the sealed tube (Experiment 287) the presence of gas pressure in the tube was revealed, the solution of the mixture in water was colored brown, and the gravimetric determination of the amount of sulfuric acid revealed a decrease instead of an increase. The sulfuric acid was lost in oxidation.

Friedel and Crafts [6] indicate that benzenedisulfonic acid begins to hydrolyze in phosphoric acid only at 300°. The indicated temperature is slightly high, and the hydrolysis of benzenedisulfonic acid can proceed at a considerably lower temperature as is seen from the data in Table 4.

PREPARATIVE PART

p-Phenolsulfonic acid was identified as the benzylisothiurea salt melting at 167°. Recrystallization failed to raise the melting point. The free p-phenolsulfonic acid fails to hydrolyze when its dilute aqueous solution is boiled for 0.5 hour in the presence of small quantities of hydrochloric acid (i.e., under the conditions of precipitating the sulfuric acid with barium chloride).

m-Phenolsulfonic acid was obtained from thrice recrystallized metanilic acid, identified as the benzylisothiurea salt with m.p. 145°.

Metanilic acid was diazotized with amyl nitrite in glacial acetic acid in the presence of excess concentrated hydrochloric acid. The solution was diluted with water, heated at 70° to termination of nitrogen evolution the amyl alcohol was extracted with benzene, and the filtered solution was evaporated in vacuo at 65°. A test sample of the obtained m-phenolsulfonic acid was heated in a dilute solution with bromide bromate and HCl at 50° for 1 hour. Here

the absence of a precipitate indicated the absence of either the ortho- or para- isomer.

The obtained p- and m-phenolsulfonic acids contained water, the amount of which was established by titrating a weighed sample with 0.1 N alkali, and by titrating with bromide-bromate solution in the cold. The results by the two methods differed by 0.5-1%. Also determined was the amount of sulfuric acid, evolved from the p- isomer in its bromination at 50°. The yield of barium sulfate was 99% of the expected.

o-Chlorobenzenesulfonic acid was obtained from orthanilic acid by the Sandmeyer reaction. Its salt was converted into the sulfonyl chloride, and then into the free acid. The amide, obtained from the chloride without recrystallization, had m.p. 182-185°.

m-Chlorobenzenesulfonic acid was obtained in a similar manner from metanilic acid. The amide had m.p. 144°.

o-Sulfobenzoic acid with m.p. 67.5° was obtained from anthranilic acid through the dithiosalicylic acid [7].

The remaining sulfonic acids were obtained either by the purification of technical products or by methods that are excellently described in the chemical literature.

SUMMARY

1. It was found that the hydrolysis of monosubstituted sulfonic acids of the benzene series, for the four investigated substituents (-OH, -Cl, -COOH, -NH₂), proceeds at a different rate depending on the position of the substituent. In all cases the kinetic stability of the isomers to hydrolysis follows the order: m > p > o.
2. The ability of p-phenolsulfonic acid to isomerize into the meta- isomer at 163° was shown.
3. The hydrolysis conditions for some of the sulfonic acids of the benzene series were shown.

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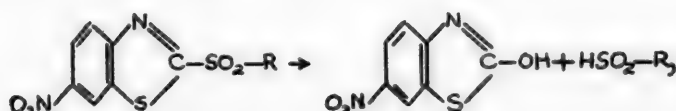
* Consultants Bureau Translation, p. 1649.

HYDROLYTIC CLEAVAGE OF ARYL AND ALKYL 2-BENZOTHAZOLYL SULFONES

II. INFLUENCE OF CERTAIN SUBSTITUTENTS ON THE RELATIVE CLEAVAGE RATE

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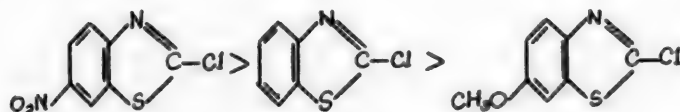
It was recently shown by us that aryl and alkyl 6-nitro-2-benzothiazolyl sulfones readily suffer hydrolytic cleavage under the influence of dilute acids and alkalis [1]. Thus, the cleavage of 6-nitro-2-benzothiazolyl 4-nitrophenyl sulfone gives 6-nitro-2-hydroxybenzothiazole (6-nitro-2-benzothiazolinone) and p-nitrobenzenesulfinic acid, i.e., the cleavage proceeds by the scheme:



where $R = O_2NC_6H_4$.

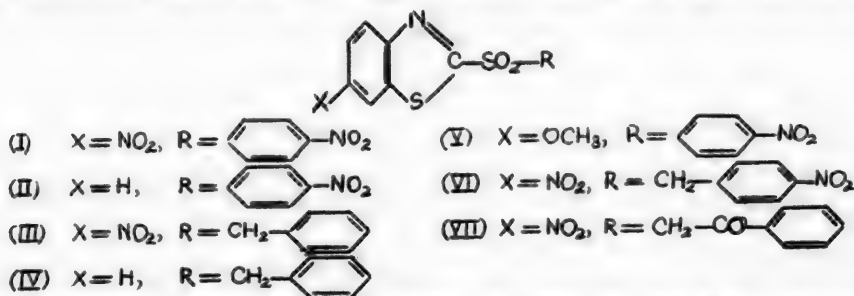
We assume that the cleavage for sulfones with other residues also proceeds in accord with this scheme.

It could be assumed that a substituent in position 6 will exert its influence on the stability of the substance as regards the hydrolytic agent. If the electron acceptor NO_2 group in position 6 will facilitate this cleavage, then the electron donor CH_3O group in the same position should retard this reaction. The opposite character of the influence of the NO_2 and CH_3O groups in position 6 of the benzothiazole ring through the conjugation chain at meso-carbon 2 ($-N=C-$ groups) can also be observed when a comparison is made of the reactivity of 2-chlorobenzothiazole versus that of 6-nitro-2-chloro- and 6-methoxy-2-chlorobenzothiazoles:



It was found that the reaction of these chlorides with the sodium salt of p-nitrothiophenol proceeds at different rates, in which connection the reactivity of the chlorine atom drops sharply from 6-nitro-2-chlorobenzothiazole to 6-methoxy-2-chlorobenzothiazole.

To establish the influence of the NO_2 and OCH_3 groups on the relative stability of the corresponding sulfones to hydrolysis, a comparison was made of the cleavage rates of compounds (I-VII) under identical conditions:



The degree of influence exerted by the mentioned NO_2 and OCH_3 groups through the conjugation chain on the bond undergoing rupture can be approximately judged by the yield of the 2-benzothiazolinone, obtained as the result of cleavage under the same periods of time. The accuracy of these determinations was $\pm 1\%$. To determine the

degree of cleavage with greater accuracy, using more exact analysis methods so as to be able to obtain the reaction rate constants, proved impossible. However, the investigation method used in this study was fully sufficient to permit judging as to the relative stability of the different compounds with respect to hydrolysis.

It was found that the cleavage of the nitro compound (I) when heated in alkaline medium on the water bath at 94° for 10 minutes was 92%, based on the isolated 6-nitro-2-benzothiazolinone. At the same time the cleavage of compound (II), not containing the NO₂ group, was roughly only 3%. A similar influence of the nitro group was also observed when the cleavage rates of compounds (III) and (IV) were compared. In alkaline medium the nitro compound (III) is completely cleaved when heated on the water bath at 94° for 60 minutes, while under the same conditions the cleavage of the compound without the NO₂ group (IV) is only 60%. In acid medium, in which the benzothiazole sulfones in general are cleaved with greater difficulty than in alkaline medium, the cleavage of substance (III) was 58% when heated for 5 hours (bath temperature 110°), while compound (IV) under the same conditions was cleaved a total of only 3%.

As regards compound (V), containing the electron donor methoxy group in position 6, then it, actually, proved to be extremely stable and practically failed to change when heated for many hours (up to 14 hours) in acid and alkaline media at 94 and 110°.

It is interesting to note that the nitro group, found in the radical R (in the p-position), exerts an influence that is opposite to that shown when it is found in position 6 of the benzothiazole ring. This can be seen from a comparison of the relative cleavage rates of compounds (III) and (VI). The cleavage rate of compound (VI) at 110°, when heated for 5 hours in acid medium, is approximately one half that of compound (III), and specifically it is 32%. Under these conditions compound (I), where the p-nitrophenyl group is directly joined to the sulfone group, is cleaved even slower (17%).

Not only a substituent in position 6 but also the radical R should exert an influence on the stability of sulfones to hydrolysis.

We studied the cleavage of alkyl 6-nitro-2-benzothiazolyl sulfones, where R is an aliphatic residue with a straight chain from C₁ to C₇ [compounds (VIII-XIV)] and of some sulfones that contained side methyl groups in the chain [compounds (XV-XIX)]. The data on these compounds are given in the Table.

Compound Number	Value of R in alkyl 6-nitro-2-benzothiazolyl sulfones	Melting point	
		Found	Indicated in the literature [2]
(VIII)	CH ₃	186-187°	186°
(IX)	C ₂ H ₅	160-161	160
(X)	C ₃ H ₇ -n	179-180	181
(XI)	C ₄ H ₉ -n	151-152	152
(XII)	C ₅ H ₁₁ -n	124-125	125
(XIII)	C ₆ H ₁₃ -n	112-113	111.5
(XIV)	C ₇ H ₁₅ -n	123-124	123.5
(XV)	CH ₂ -CH-CH ₃ CH ₃	122-123	124
(XVI)	CH ₂ -CH ₂ -CH-CH ₃ CH ₃	112-113	115
(XVII)	CH ₂ -CH ₂ -CH ₂ -CH-CH ₃ CH ₃	120-121	-
(XVIII)	CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH-CH ₃ CH ₃	135-136	-
(XIX)	CH-CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₃ CH ₃	115-116	-
(XX)	CH ₂ -COOC ₂ H ₅	134	-

It was found that the cleavage rate is significantly retarded with increase in chain length; thus, for example, if sulfone (VIII), where R = CH₃, is 90% cleaved when heated in acid medium at 94° for 60 minutes, then sulfone (XII), where R = C₅H₁₁, is cleaved a total of only 1%, while sulfone (XIV), where R = C₇H₁₅, is not cleaved at all (however, its cleavage to the extent of 96% was achieved by heating in an alkaline medium for 20 minutes at 94°; with R = CH₃ the cleavage under the same conditions and for the same length of time is already complete at 60°).

Especially noteworthy is the ease of cleavage of compounds (XX), where $R = CH_2 - C \begin{matrix} \nearrow O \\ \searrow OC_2H_5 \end{matrix}$, and (VII), where $R = CH_2 - C \begin{matrix} \nearrow O \\ \searrow \text{Cyclohexyl} \end{matrix}$, i.e., compounds in which a carbonyl group is found in the beta-position to the sulfone group.

In these compounds cleavage in alkaline medium already proceeds in a matter of several minutes with slight heating (up to 40°). Apparently, here the cleavage also proceeds at the linkages of the methylene group with the sulfone and carbonyl groups, similar to the situation that exists in the hydrolytic cleavage of 1,3-diketones.

EXPERIMENTAL*

The sulfides used for the synthesis of the sulfones were obtained by reacting the corresponding alkyl halides with mercaptobenzothiazole, using the method described in [2]. The sulfones were obtained from the sulfides in yields of 80-85% by the oxidation with 7.5% $KMnO_4$ solution in glacial acetic acid, using the method described in the literature [1,2].

1. 2-Benzothiazolyl 4-Nitrophenyl Sulfone (II). The starting 2-benzothiazolyl 4-nitrophenyl sulfide is described in the literature [3]; it was obtained by the reaction of 2-mercaptobenzothiazole with p-chloronitrobenzene. This sulfide is more readily obtained by heating 2-chlorobenzothiazole in alcohol solution with the sodium salt of p-nitrothiophenol.

Two grams of 2-chlorobenzothiazole was dissolved in 50 ml of ethyl alcohol. To this solution was added a solution of 2 g of p-nitrothiophenol in 50 ml of alcohol and 60 ml of 2 N NaOH. After heating for 2.5 hours and subsequent cooling there separated yellow platelets from the reaction mixture. Yield 1.20 g (34%). M.p. 112-113° (literature 111.5-112.5° [3]). Oxidation with 7.5% $KMnO_4$ solution gave the sulfone with m.p. 213-214° (literature 207-208° [3]) in 90% yield.

2. 2-Benzothiazolyl Benzyl Sulfone (IV). The sulfone was obtained in 65% of the theoretical yield by the oxidation of the sulfide, described earlier [4]. After recrystallization from dilute alcohol the sulfone was obtained as glistening colorless platelets with m.p. 105-106°.

5.100 mg sub.: 0.225 ml N_2 (24°, 732 mm). Found %: N 4.88. $C_{14}H_{11}O_2NS_2$. Calculated %: N 4.84.

3. 6-Methoxy-2-Benzothiazolyl 4-Nitrophenyl Sulfone (V). The corresponding, not known, sulfide was obtained by the condensation of 2-chloro-6-methoxybenzothiazole [5] with the sodium salt of p-nitrothiophenol with the addition of KI in boiling butyl alcohol medium. The sulfide had m.p. 128-130°. Yield 28%. The sulfone, obtained in 82% yield by the oxidation of the sulfide, after recrystallization from butyl alcohol had m.p. 247-248°.

The sulfone is soluble in hot butyl alcohol, readily soluble in acetone, and difficultly soluble in alcohol.

4.235 mg sub.: 0.318 ml N_2 (27°, 738 mm). 4.130 mg sub.: 0.314 ml N_2 (28°, 739 mm). 0.0352 g sub.: 6.057 ml 0.1 N $Na_2S_2O_3$. Found %: N 8.29, 8.39; OCH_3 8.89. $C_{14}H_7O_4N_2S_2(OCH_3)$. Calculated %: N 7.89; OCH_3 8.86.

4. 6-Nitro-2-Benzothiazolyl 4'-Methylamyl Sulfone (XVII). The corresponding sulfide with m.p. 45-49° was dissolved in glacial acetic acid and oxidized with a 7.5% aqueous $KMnO_4$ solution. The sulfone from the reaction, after recrystallization from ethyl alcohol, was obtained as slightly yellow needles with m.p. 120-121°. The sulfone is readily soluble in acetone and in hot alcohol.

3.140 mg sub.: 0.255 ml N_2 (26°, 732 mm). Found %: N 8.92. $C_{13}H_{10}O_4N_2S_2$. Calculated %: N 8.52.

5. 6-Nitro-2-Benzothiazolyl 5'-Methylhexyl Sulfone (XVIII). The sulfone, obtained by the oxidation of the oily sulfide, after recrystallization from alcohol was obtained as glistening colorless transparent leaflets, melting at 135-136°.

5.970 mg sub.: 0.421 ml N_2 (24°, 736 mm). Found %: N 7.85. $C_{14}H_{18}O_4N_2S_2$. Calculated %: N 8.17.

6. 6-Nitro-2-Benzothiazolyl 1'-Methylheptyl Sulfone (XIX). The sulfide with m.p. 107° was oxidized with permanganate to the sulfone in 75% yield. After recrystallization from alcohol the sulfone was obtained as silky, slightly

* Preparation directions are only given for the sulfones that are not described in the literature. Compounds (I, III, VI, VII) were described earlier [1].

yellow needles with m.p. 115-116°.

4.955 mg sub.: 0.343 ml N₂ (25°, 730 mm). Found %: N 7.62. C₁₅H₂₀O₄N₂S₂. Calculated %: N 7.86.

7. 6-Nitro-2-Benzothiazolyl Propionyloxymethyl Sulfone (XX). 6-Nitro-2-mercaptobenzothiazole (2.65 g) was dissolved in 25 ml of alcohol, and to this solution was added 6.3 ml of 2 N NaOH and 1.6 g of KI. The mixture was brought to a boil, and to it was added 5.5 ml of ethyl chloroacetate. After heating for 2 hours under reflux the mixture was poured into ice water. The initially obtained oil crystallized on standing. The crystals were recrystallized from methyl alcohol. Yellow needles, m.p. 97°. Yield 1.95 g (54%).

The sulfide is readily soluble in methyl and ethyl alcohols, acetone and hot carbon tetrachloride.

4.690 mg sub.: 0.375 ml N₂ (21°, 748 mm). 5.500 mg sub.: 0.459 ml N₂ (21°, 748 mm). Found %: N 9.14, 9.54. C₁₁H₁₀O₄N₂S₂. Calculated %: N 9.39.

Oxidation of the sulfide with KMnO₄ gave the sulfone. After recrystallization from alcohol the sulfone was obtained as slender colorless needles with m.p. 134° and in 60% yield. The sulfone is soluble in hot methyl and ethyl alcohols, and is extremely soluble in acetone.

5.025 mg sub.: 0.382 ml N₂ (21°, 744 mm). 4.990 mg sub.: 0.363 ml N₂ (22°, 744 mm). Found %: N 8.64, 8.39. C₁₁H₁₀O₆N₂S₂. Calculated %: N 8.49.

SUMMARY

1. It was shown that the electron acceptor nitro group in aryl 6-nitro-2-benzothiazolyl sulfones (I, III) lowers the stability of the sulfone toward hydrolysis (in both acid and alkaline media), while, in contrast, the electron donor methoxy group in the aryl 6-methoxy- sulfone (V) raises it significantly.

2. The relative hydrolytic cleavage rate for sulfones with aliphatic radicals steadily diminishes with increasing chain length in going from the lower to the higher members of a homologous series.

3. Several new aryl and alkyl benzothiazolyl sulfones are described in this study.

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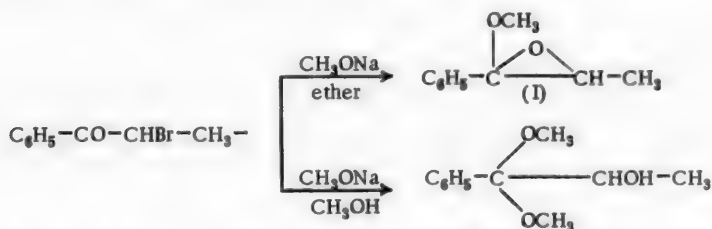
ANOMALOUS REACTIONS OF α -BROMO KETONES

IV. Reaction of Sodium Phenolate with α -Bromoethyl Phenyl Ketone

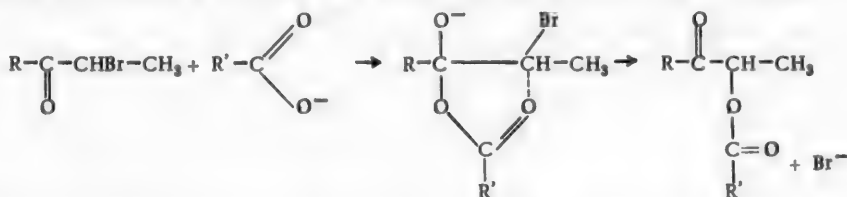
T. Temnikova and S. Myukhyurdari

Apparently, in the action of nucleophilic reagents on α -bromo ketones, in particular the sodium alcoholates and the salts of organic acids, the reagent in all cases first reacts with the carbon atom of the carbonyl group in the bromo ketone [1]. However, the structure of the final reaction products depends on the process conditions and on the nature of the operating reagent.

The action of sodium methylate on the α -bromoalkyl phenyl ketones in anhydrous ether gives the α -methoxy oxides (I) [2]; if methyl alcohol is used as the reaction medium the dimethyl ketals of the keto alcohols are obtained, formed as the result of the methoxy oxides reacting with the solvent [3].



On the other hand, the reaction of α -bromo ketones with the salts of organic acids results in the formation of keto alcohol esters, corresponding to the bromo ketone; only in rare cases in these reactions is the formation of esters, corresponding to the isomeric keto alcohol, observed, which points to the probability in these cases that the anions of the acids first react with the carbonyl group of the bromo ketone. It is very probable that also in normal substitution reactions the first stage of the reaction is that of the acid anion with the carbon of the carbonyl group, with subsequent rearrangement of the molecule in the cleavage of the bromide ion, in accord with the scheme:



Analogous intermediate products were assumed earlier many times for explaining the intramolecular migrations of acyl groups [4], and also for explaining the formation of isomeric keto alcohols in the methanolysis of keto alcohol esters [5].

It appeared of interest to study the reaction between sodium phenolate and the α -bromo ketones under different conditions, since phenol, as a nucleophilic reagent, is weaker than the alcohols and stronger than the acids; on the other hand, in contrast to the acids, phenol does not contain two oxygen atoms and, in the case of primary formation of the addition product, the latter cannot undergo intramolecular transformation in accord with the scheme proposed for the addition products of acid anions.

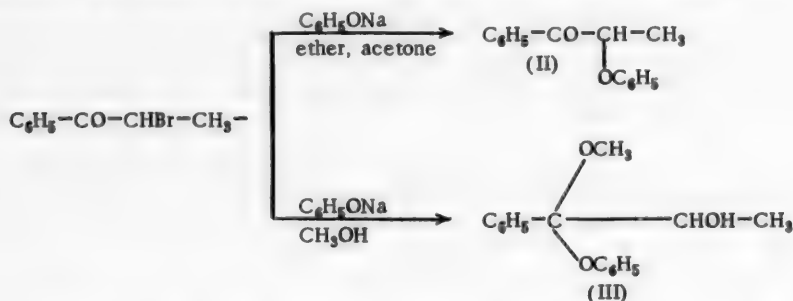
In the literature only several examples of the reaction of bromo ketones with sodium phenolate are described [6]; in all cases α -phenoxy ketones are obtained, the structures of which were not specially proven.

In the present work we studied the reaction between sodium phenolate and α -bromoethyl phenyl ketone in anhydrous ether and in methyl alcohol. It was found that the direction of the reaction depends on the solvent. It was observed that basically tar formation results when the reaction is carried out in anhydrous ether, and only in insignificant amount was it possible to isolate the α -phenoxy ketone, obtained earlier by Bradsher and Rosner [7] in the reaction of

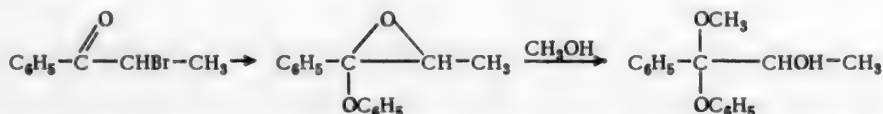
these same compounds in acetone solution. The structure of the phenoxy ketone as being a derivative of methylbenzoylcarbinol was proved by way of determining its ultraviolet absorption spectrum: the curve had two maxima, characteristic for the benzoyl grouping at λ_{272} and $328 \text{ m}\mu$. Further proof of the structure was made by way of converting the compound into the monophenyl ether of 1,1-diphenyl-1,2-propanediol with m.p. 134° , obtained earlier by Stoermer and Riebel from the methyl ester of phenoxypropionic acid and phenylmagnesium bromide [8].

When the reaction between sodium phenolate and α -bromoethyl phenyl ketone was carried out in methyl alcohol a different reaction product was obtained – the ketal of methylbenzoylcarbinol (α -methoxy- α -phenoxybenzylmethylcarbinol) (III).

The structure of the latter was proved by its hydrolysis to methylbenzoylcarbinol.

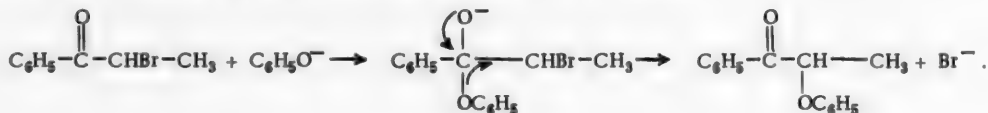


As a result, it was shown that in the reaction of sodium phenolate with α -bromoethyl phenyl ketone, in ether solution the reaction proceeds in the same manner as with the salts of organic acids, – in the direction of forming the ethers of the keto alcohol; when methyl alcohol is used as the reaction medium the process proceeds the same as with the alcoholates, – in the direction of forming ketals. It is possible that ketal formation proceeds in accord with the following scheme:



In connection with this it appeared of interest to study the reaction of the methyl lactolide of methylbenzoylcarbinol (I) with phenol. The reaction was run in benzene, and here the only product isolated was the ketal (III).

It is possible that the formation of the phenoxy ketone also proceeds through the stage of primary reaction of the phenolate ion with the carbon of the carbonyl group, in accord with the scheme:



EXPERIMENTAL

Action of Sodium Phenolate on α -Bromoethyl Phenyl Ketone

a) In Diethyl Ether Medium. To the dry sodium phenolate, prepared from 12 g of metallic sodium and suspended in dry ether, was slowly added with constant stirring an ether solution of 30 g of α -bromoethyl phenyl ketone. On conclusion of reaction the excess sodium phenolate and formed sodium bromide were filtered, while the ether was distilled off; the residue was a heavy dark brown tar. An attempt to isolate the substance by vacuum distillation only led to pronounced swelling. We were able to extract the reaction product by heating it with petroleum ether, in which the tar proved to be almost insoluble. Cooling of the extract gave colorless crystals, which were repeatedly recrystallized from petroleum ether. Yield 2.5 g, m.p. 76° .

Found %: C 79.40, 79.38; H 6.14, 6.10. M 220.9. $\text{C}_{15}\text{H}_{14}\text{O}_2$. Calculated %: C 79.62; H 6.19. M 226.

b) In Methyl Alcohol Medium. To a solution of sodium phenolate, prepared by dissolving 5 g of sodium in methyl alcohol with the subsequent addition of 21 g of phenol, was added 10 g of α -bromoethyl phenyl ketone, and the solution was heated with constant stirring to complete reaction. The sodium bromide precipitate was filtered, from the fil-

trate the alcohol was distilled off on the water bath, the residual oil was extracted with ether, and the ether solution was washed with water and alkali. After distilling off the ether the residual solid reaction product was recrystallized from petroleum ether. Colorless crystals with m.p. 124° were obtained.

0.1092 g sub.: 0.2970 g CO₂; 0.0700 g H₂O. 0.1056 g sub.: 0.2870 g CO₂; 0.0680 g H₂O. 0.0318 g sub.: 7.83 ml 0.1 N Na₂S₂O₃. 0.0380 g sub.: 9.1 ml 0.1 N Na₂S₂O₃. 0.0528 g sub.: 5 ml CH₄ (14°, 748 mm). 0.0516 g sub.: 5.1 ml CH₄ (14°, 748 mm). 0.1395 g sub.: 18.28 g benzene: Δt 0.155°. Found %: C 74.23, 74.14; H 7.17, 7.20; OCH₃ 12.7, 12.1; act. H 1.00, 1.02. M 251. C₁₆H₁₈O₃. Calculated %: C 74.41; H 6.97; OCH₃ 12.0; act. H 1. M 258.

Preparation of the Monophenyl Ether of 1,1-Diphenyl-1,2-Propanediol

To a solution of phenylmagnesium bromide, prepared from 4 g of Mg and 18 ml of bromobenzene, was added an ether solution of 3 g of phenoxypropionphenone. After decomposing the organomagnesium complex with water and distilling off the ether from the ether extract the residue was subjected to steam distillation for the purpose of removing benzene, bromobenzene and diphenyl. The substance, which congealed on cooling, was dried and recrystallized from ethyl alcohol. M.p. 133-134°, yield 3.6 g.

The substance is difficultly soluble in hot alcohol, poorly soluble in petroleum ether, and relatively soluble in benzene.

Found %: C 83.27; H 6.20; act. H 0.98. C₂₁H₂₀O₂. Calculated %: C 83.16; H 6.27; act. H 1.

Action of Sulfuric Acid on the Monophenyl Ether of 1,1-Diphenyl-1,2-propanediol. Dilute sulfuric acid even on heating to the boil fails to act on the ether. On heating with 60% sulfuric acid nearly to the boil the substance melted; heating at this temperature with constant stirring was continued for 2 hours. The reaction product (an oil with a strong odor of phenol) was extracted with ether, the ether solution was washed with alkali, and dried over Na₂SO₄. After distilling off the ether an oil remained, the crystallization of which we were able to achieve by the addition of 1 ml of alcohol. After recrystallization from alcohol the substance melted at 58° and failed to show a depression when mixed with unsymmetrical diphenylacetone.

The semicarbazone of the obtained substance was identical with the semicarbazone of unsymmetrical diphenylacetone (m.p. 167-169°), the mixed melting point was the same.

Action of Phenol on the Methyl Lactolide of Methylbenzoylcarbinol

To the freshly prepared methyl lactolide of methylbenzoylcarbinol (α-methoxy-α-phenyl-β-methylethylene oxide) with b.p. 62-64° at 2-2.5 mm, diluted with a double volume of dry benzene, was added a benzene solution of phenol (7 g of phenol for 7 g of oxide). The solution was allowed to stand overnight at room temperature. Colorless crystals were obtained from the reaction, yield 6.2 g. The substance is readily soluble in ether and chloroform, in benzene and alcohol on heating, and crystallizes well from petroleum ether. M.p. 123-124°.

Found %: OCH₃ 12.0; act. H 1.09. M 249. C₁₆H₁₈O₃. Calculated %: OCH₃ 12.0; act. H 1. M 258.

The mixed melting point with the substance, obtained by the action of sodium phenolate on α-bromoethyl phenyl ketone in methyl alcohol solution, was not depressed.

Hydrolysis of the Substances. The substances (4.5 g) were added gradually and with vigorous stirring to a solution of 50 ml of alcohol and 20 ml of 5% H₂SO₄. After complete solution of the substances the alcohol was removed by vacuum distillation, water was added to the residual substance and the reaction product was extracted with ether; from the ether solution the phenol formed as the result of hydrolysis was extracted by washing with alkali and then identified as the trifluorophenol with m.p. 157-158°. The substance remaining in the ether solution was identified as methylbenzoylcarbinol by converting it with the aid of phenylmagnesium bromide into the glycol - 1,1-diphenyl-1,2-propanediol with m.p. 94°; the mixed melting point with the authentic glycol failed to show a depression.

SUMMARY

1. The reaction of α-bromoethyl phenyl ketone with sodium phenolate in diethyl ether medium gave α-phenoxyethyl phenyl ketone; the same reactants in methyl alcohol medium gave the mixed ketal of methylbenzoylcarbinol - α-methoxy-α-phenoxybenzylmethylcarbinol.

2. The action of phenol on the methyl lactolide of methylbenzoylcarbinol gave the ketal of methylbenzoylcarbinol - α-methoxy-α-phenoxybenzylmethylcarbinol.

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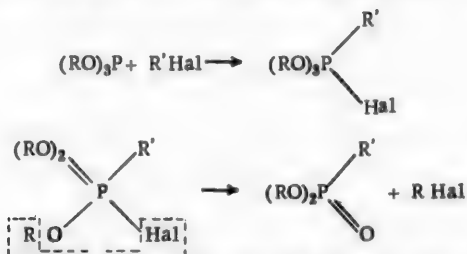
Leningrad State University

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MECHANISM OF THE ARBUZOV REARRANGEMENT REACTION OF α, β -DIBROMODIETHYL ETHER WITH PHOSPHITES

V. S. Abramov and G. A. Karp

In 1905 Arbuzov [1] discovered a remarkable reaction for the conversion of phosphorous acid esters, under the influence of alkyl halides, into the esters of alkylphosphinic acids. The following scheme was given for the reaction:

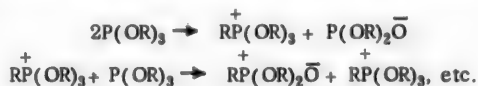


Arbuzov's scheme is supported by the reaction for the action of alkyl halides on the esters of phosphorous acid, the alkyl radicals of which are different. As a result the ester of an alkylphosphinic acid is obtained, the alkyl radical of which corresponds to the alkyl halide taken. Also in support of the scheme is the addition product of methyl iodide to the phenyl ester of phosphorous acid, obtained by Michaelis and Kaehne [2] and decomposed by Arbuzov in accord with the scheme. For more than fifty years the addition product of methyl iodide to triphenyl phosphite has been the solitary example supporting the formation of monoacid halo-esters of orthophosphinic acids.

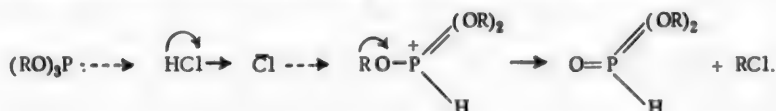
Arbuzov and Nesterov [3] obtained a number of crystalline products by the addition of alkyl iodides to triphenyl phosphite and studied the isomerization rate of phosphorous acid esters as a function of the size and structure of the radicals. The obtained results support the conclusions made earlier by Arbuzov that the Arbuzov reaction proceeds in two stages [4].

The kinetics for the isomerization of phosphorous acid esters was investigated by Staronka [5], who found that this process is autocatalytic.

Rumpf [6] believes that the isomerization reaction can proceed in the absence of alkyl halides by the following chain sequence:



It was shown by Gerrard and Green [7] that as the result of reacting hydrogen chloride, ethyl iodide and acetyl chloride with tri-2-octyl phosphite, prepared from (+)-2-octanol, the corresponding inverted (-)-2-chloro and (-)-2-iodooctanes are obtained. A Walden inversion takes place in the process of transforming the phosphites. On this basis they proposed the following scheme for explaining the mechanism of the reaction:



Pudovik [8] studied the action of phosphorous trichloride on primary and secondary ethoxypentenols and butenols and obtained a definite proportion of the corresponding primary and secondary chlorides, from both the primary and secondary alcohols. The obtained results differed from those obtained in the action of hydrogen chloride on the ethoxypentenols and butenols. In the opinion of the author, the latter reaction proceeds with allylic rearrangement. Taking into consideration the different results of these reactions and the fact that up to now the addition products of alkyl halides with aliphatic phosphites had not been obtained, Pudovik believes it possible to give an explanation for the

mechanism of the Arbuzov rearrangement, for which he postulates: in the reaction of phosphorous trichloride with ethoxypentenols and butenols the allyl rearrangement is absent, that this reaction proceeds through the formation of phosphites, and that the subsequent formation of halo derivatives proceeds through the Arbuzov reaction. However, neither phosphites, nor dialkylphosphorous acids, nor any other substances, containing phosphorus, were isolated. In addition, the phosphorus containing part of the reaction does not figure in the experiment.

The proposed explanation for the mechanism of the Arbuzov reaction agrees with that offered by Gerrard [7]. Together with the inverted halo derivatives, Gerrard also obtained the esters of alkylphosphinic acids or dialkylphosphorous acids, which dealkylated very slowly due to the absence of a solitary pair of electrons for the phosphorous. Such behavior for these compounds ensues from the numerous investigations made by Arbuzov [1,9], who assigns the dialkylphosphorous acids as having pentavalent phosphorous in their structure.

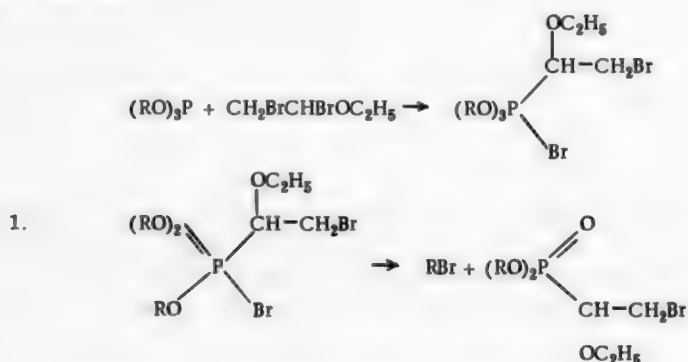
The dialkylphosphorous acids were not obtained in Pudovik's experiments. This circumstance is explained by a new assumption that the dialkylphosphorous acids are much more reactive than the dialkylphosphorous acids, although the reason for the easy reaction of the dialkylphosphorous acids with hydrogen chloride in the absence of a solitary pair of electrons for the phosphorous remains incomprehensible. A scheme for the dealkylation of dialkylphosphorous acids was not given. Kamai and Shugurova [10], in reacting phosphorous trichloride with allyl alcohol under ordinary conditions, obtained dialkylphosphorous acid, which was characterized by them from all angles.

In our opinion [11] the conclusions made by Pudovik fail to follow from the experimental material presented by him, but instead are purely speculative, since the intermediate products predicted by his scheme are not confirmed. Apparently, other methods for explaining the course of this reaction can be proposed with equal success. Pudovik expands this particular case to the Arbuzov rearrangement in general; he extrapolates it to the completely unstudied tertiary phosphites [12], which to us appears completely unwarranted and not ensuing from his experiments.

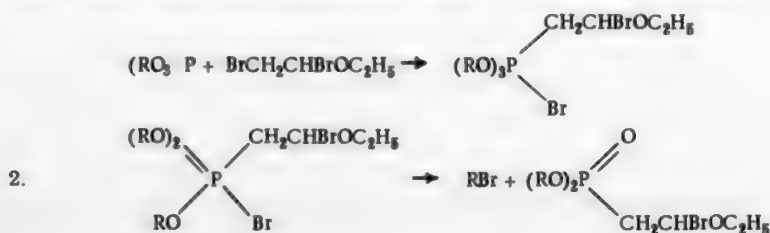
In the present study it was shown that the Arbuzov rearrangement for also the aliphatic phosphites proceeds with the formation of an intermediate addition product, i.e., it proceeds in two different independent stages. Although the addition product was not isolated chemically pure, still conclusive evidence of its formation was demonstrated by a series of indirect observations. This first noted instance of separate progress for both stages of the Arbuzov reaction for aliphatic phosphites is of interest for the reason that Arbuzov [1] believed that the addition products were "incapable of existence", while Kosolapoff [13] states that "they decompose spontaneously, and it is necessary to distill only the mixture of obtained final products".

Arbuzov and Grechkin [14] were able to isolate the addition product of methyltin triiodide with triethyl phosphite.

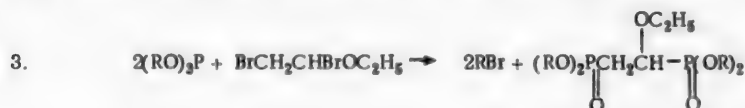
We studied the action of α, β -dibromodiethyl ether on phosphites. In theory the reaction can proceed in three possible directions:



where the α -bromo atom of α, β -dibromodiethyl ether reacts with the phosphite.



where the β -bromo atom of α, β -dibromodiethyl ether reacts with the phosphite.



where both of the bromine atoms of α, β -dibromodiethyl ether react with the phosphite.

For the reaction the reactants were taken in equimolar amounts, for which reason we could hardly expect the reaction to take place in accord with scheme 3.

On the basis of the studies made [15] on the synthesis of hydrocarbons with the aid of α, β -dibromodiethyl ether, where it was shown that the latter reacts with organomagnesium compounds at the α -bromo atom, which appears to be the more active, we assumed that with phosphites also the α, β -dibromodiethyl ether reacts at the α -bromo atom, i.e., the reaction proceeds in accord with Scheme 1, and no further investigations of the structure of the obtained products were made.

The experiments on the action of α, β -dibromodiethyl ether on phosphites were made under the usual conditions [4], i.e., on heating to 120-150° it was revealed that the reaction is exceedingly violent and leads to resinification of the reaction products. Then the experiments were run at room temperature. The course of the reaction can be followed by the change in the odor of the reactants and the change in physical constants. As easily determined constants we chose the index of refraction and specific gravity.

The experiments were run in flasks with ground-glass stoppers. The starting products — α, β -dibromodiethyl ether and the phosphites — were freshly distilled. The constants were determined immediately after the products, cooled to -10°, were poured together. The measurement results are summarized in Table 1.

The data in Table 1 show that in all of the cases studied by us the index of refraction steadily decreases with time, while the specific gravity steadily increases. At the same time there occurs almost complete disappearance of the odor, characteristic for phosphites, and the sharp odor, attacking the eyes and nose, of α, β -dibromodiethyl ether. This gives us the right to affirm that α, β -dibromodiethyl ether does add to phosphites.

TABLE 1

Variation in the Physical Constants for Reaction Mixtures of α, β -Dibromodiethyl Ether n_D^{20} 1.5012, d_4^{20} 1.7658 with Trialkyl Phosphites and the Constants of the Original Substances at 17-20°

Time (in days)	n_D^{20}	d_4^{20}	n_D^{20}	d_4^{20}	n_D^{20}	d_4^{20}	n_D^{20}	d_4^{20}
	Trimethyl Phosphite		Triethyl Phosphite		Tributyl Phosphite		Triisobutyl Phosphite	
	1.4093	1.0493	1.4158	0.9687	1.4318	0.9133	1.4266	0.9036
	Reaction Mixture		Reaction Mixture		Reaction Mixture		Reaction Mixture	
0	1.4572	1.4050	1.4512	1.2532	1.4548	1.2068	1.4502	1.1750
1	1.4565	1.4230	1.4494	1.2646	1.4524	1.2095	1.4493	1.1786
2	1.4560	1.4447	1.4468	1.3002	1.4502	1.2103	1.4482	1.1857
3	1.4560	1.4445	1.4468	1.3025	—	—	1.4468	1.1930
4	1.4560	1.4447	1.4462	1.3042	1.4507	—	1.4462	1.1924
5	—	—	1.4462	1.3052	1.4507	1.2170	—	—
6	—	—	1.4462	1.3052	1.4509	1.2168	—	—
7	—	—	—	—	—	—	1.4462	1.1946
10	1.4560	1.4448	—	—	1.4507	1.2165	1.4462	1.1962
11	—	—	—	—	1.4506	1.2170	—	—
13	—	—	—	—	—	—	1.4462	1.1960
36	—	—	1.4460	1.3054	—	—	—	—
40	—	—	—	—	—	—	1.4462	1.1965
43	—	—	—	—	1.4507	1.2174	—	—

That reaction takes place is also indicated by the fact that the temperature rises on mixing the reactants. Thus, for example, on mixing trimethyl phosphite with α, β -dibromodiethyl ether, both of which had first been cooled to -3°, the temperature rose from -3° to +7°, and after vigorous shaking to 35° in 5 minutes. The heat effect is diminished with increase in the size of the phosphite radical. That a reaction takes place is also indicated by the fact that the re-

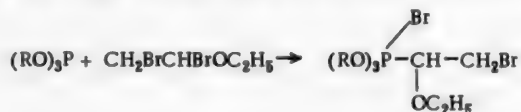
actant mass suffers a noticeable contraction in volume; unfortunately, we failed to make any quantitative dilatometric determinations. If the constancy of the established index of refraction and specific gravity is taken as a criterion of reaction, then it follows that the reaction at room temperature (17-20°) is completed in 3-5 days. The α, β -dibromodiethyl ether addition products are colorless, heavy, viscous liquids. Proceeding from the averages of the last determinations of the index of refraction and specific gravity we made an attempt to find the molecular refractions of the addition products and compare them with the calculated values. • The results are given in Table 2.

As follows from Table 2, the calculated and found molecular refractions fail to agree, in which connection the calculated values are always higher. Such lack of agreement can be explained by the fact that the obtained products are not chemically pure substances, or by the fact that the atomic refraction of phosphorus in these compounds is different. We attempted to obtain the addition products from α, β -dibromodiethyl ether with the phosphites in chemically pure form by crystallizing them. For this we cooled the products with liquid air, trying to obtain them in the crystalline state; however, it was revealed that the products fail to crystallize, either in the free state or in solution, but instead become hard and glassy.

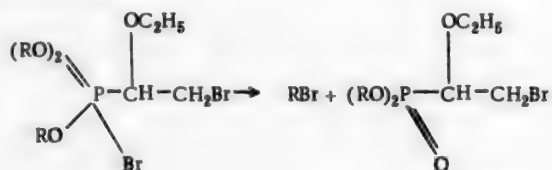
TABLE 2

Exp. No.	Formula	n_D^{20}	d_4^{20}	MR_D	
				Calculated	Found
1	$\begin{array}{c} \text{Br} \\ \\ (\text{CH}_3\text{O})_3\text{P}-\text{CH}-\text{CH}_2\text{Br} \\ \\ \text{OC}_2\text{H}_5 \end{array}$	1.4560	1.4446	64.77	66.99
2	$\begin{array}{c} \text{Br} \\ \\ (\text{C}_2\text{H}_5\text{O})_3\text{P}-\text{CH}-\text{CH}_2\text{Br} \\ \\ \text{OC}_2\text{H}_5 \end{array}$	1.4462	1.3052	78.05	81.30
3	$\begin{array}{c} \text{Br} \\ \\ (\text{C}_4\text{H}_9\text{O})_3\text{P}-\text{CH}-\text{CH}_2\text{Br} \\ \\ \text{OC}_2\text{H}_5 \end{array}$	1.4507	1.2170	105.76	106.54
4	$\begin{array}{c} \text{Br} \\ \\ \text{iso}-(\text{C}_4\text{H}_9\text{O})_3\text{P}-\text{CH}-\text{CH}_2\text{Br} \\ \\ \text{OC}_2\text{H}_5 \end{array}$	1.4462	1.1963	105.76	107.48

All of the above clearly shows that we had obtained the addition products of α, β -dibromodiethyl ether with aliphatic esters and had realized, as a result, the first stage of the Arbuzov rearrangement:



If this is so, then the products obtained by us should be capable of decomposition (in accord with the scheme proposed by Arbuzov) into alkyl bromides and the esters of α -ethoxy- β -bromoethylphosphinic acid; in other words, the second stage of this reaction can be run separately:



• The atomic refraction for phosphorous was taken from the compound $\text{R}-\text{P}(=\text{O})(\text{OR})\text{Cl}$ and is equal to 4.270.

Actually, on heating to 60-140° the addition products obtained by us from α,β -dibromodiethyl ether and the aliphatic esters of phosphorous acid, the corresponding alkyl bromides are split off in yields of 80-85%, the constants of which agree well with the literature data, and the esters of α -ethoxy- β -bromoethylphosphinic acid are obtained.

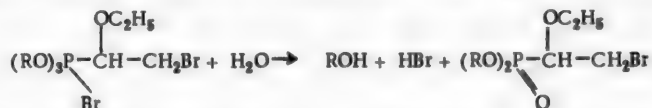
That in the heating decomposition actually takes place with the cleavage of the alkyl halide, and not just simple distillation of the already cleaved alkyl halide found in the mixture, as is postulated by Kosolapoff [13], is indicated by the fact that a vacuum is formed if the addition product is placed in a flask and connected to the vacuum without heating, i.e., at room temperature. However, the vacuum is immediately destroyed if we only heat the flask to the point of incipient decomposition. The vacuum is again restored only when all of the alkyl bromide has been evolved, after which it becomes possible to distill the ester of α -ethoxy- β -bromoethylphosphinic acid. The constants of the obtained esters of α -ethoxy- β -bromoethylphosphinic acid are given in Table 3.

TABLE 3

Physical Constants of the Esters of α -Ethoxy- β -bromoethylphosphinic Acid

Exp. No.	Formula	Boiling point	n_D^{20}	d_4^{20}	MR _D		Amt. of phosphorus (in %)		Yield (in %)
					Calculated	Found	Calculated	Found	
1	$(CH_3O)_2P(=O)-CH(OC_2H_5)-CH_2Br$	137-138° (13 mm)	1.4648	1.4402	49.68	50.08	11.87	11.51, 11.70	60.4
2	$(C_2H_5O)_2P(=O)-CH(OC_2H_5)-CH_2Br$	140-140.5 (9 mm)	1.4570	1.3180	58.91	59.73	10.72	10.53, 10.40	74.1
3	$(C_4H_9O)_2P(=O)-CH(OC_2H_5)-CH_2Br$	176-178 (12 mm)	1.4548	1.1909	77.38	78.61	8.98	9.00, 8.99	52.3
4	iso- $(C_4H_9O)_2P(=O)-CH(OC_2H_5)-CH_2Br$	170-171 (14 mm)	1.4523	1.1839	77.38	78.66	8.98	9.19, 8.90	53.2
5	$(C_6H_5O)_2P(=O)-CH(OC_2H_5)-CH_2Br$	M.p. 40-42°	-	-	-	-	8.05	8.45, 8.30	-

The addition products of α,β -dibromodiethyl ether with aliphatic phosphites, analogous to the addition product from methyl iodide and triphenyl phosphite, obtained by Michaelis and Kaehne [2], are decomposed by water:



The esters of α -ethoxy- β -bromoethylphosphinic acid are isolated from the decomposition products, the constants of which are identical with the constants of the esters obtained by thermal decomposition. The second stage of the Arbuzov rearrangement was performed separately with these two reactions.

Bromomethyl n-propyl ether also reacts with triethyl phosphite with the formation of an addition product, and the reaction proceeds in two separate stages.

All of the above gives us the right to conclude that the scheme proposed by Arbuzov for explaining this reaction remains general. The first stage of the reaction, undoubtedly, proceeds by the bimolecular mechanism. In the second stage there proceeds either intramolecular decomposition of the addition product or its ionization and subsequent

cleavage of the alkyl halide by the bimolecular mechanism. It seems to us that intramolecular decomposition is possible here, although for its verification a study of the structure of the addition product and the kinetics of its decomposition would be required.

From the obtained esters of α -ethoxy- β -bromoethylphosphinic acid a mole of hydrogen bromide was removed by an alcoholic potassium hydroxide solution with cooling [17]. The esters of α -ethoxyvinylphosphinic acid were obtained as a result. The constants of the obtained esters are given in Table 4.

TABLE 4
Physical Constants of Some Esters of α -Ethoxyvinylphosphinic Acid

Exp. No.	Formula	Boiling point	n_D^{20}	d_4^{20}	MR_D		Phosphorus content (in %)		Yield (in %)
					Calculated	Found	Calculated	Found	
1	$(CH_3O)_2P(=O)-C(=CH_2)OC_2H_5$	122-123° (10 mm)	1.4462	1.1702	41.44	41.05	17.22	17.10, 16.92	75.3
2	$(C_2H_5O)_2P(=O)-C(=CH_2)OC_2H_5$	128 (10 mm)	1.4408	1.0930	50.67	50.21	14.90	14.80, 14.65	76.6
3	$(C_4H_9O)_2P(=O)-C(=CH_2)OC_2H_5$	164-166 (13 mm)	1.4426	1.0182	69.15	68.75	11.74	11.40, 11.51	79.1
4	iso- $(C_4H_9O)_2P(=O)-C(=CH_2)OC_2H_5$	148-149 (10 mm)	1.4378	0.9954	69.15	69.44	11.74	11.21, 11.45	77.2

EXPERIMENTAL

Preparation of the Addition Product of α, β -Dibromodiethyl Ether with Trimethyl Phosphite. The reaction was carried out in a ground-glass stoppered flask, in which 18 g of freshly distilled trimethyl phosphite (b.p. 110-111°, n_D^{20} 1.4093) was placed. The flask was cooled to -3°, after which an equimolar amount of 34 g of α, β -dibromodiethyl ether (b.p. 72-74° at 15 mm, n_D^{20} 1.5012), also cooled to -3°, was added. Immediately after mixing the constants and temperature were measured, which proved to be: 7°, n_D^{20} 1.4572 and d_4^{20} 1.4050. Then, after vigorous shaking, the temperature was raised to 35° in 5 minutes, while n_D^{20} 1.4565, d_4^{20} 1.4230.

The further course of the reaction was controlled by the change in the coefficient of refraction and specific gravity. The reaction mixture was maintained at 17-19°. The observation results are given in Table 1.

After several days the odors of trimethyl phosphite and α, β -dibromodiethyl ether disappeared almost completely. The volume of the reactant mixture was noticeably diminished.

The molecular refraction was calculated from the obtained data:

n_D^{20} 1.4560, d_4^{20} 1.4446, MR_D 66.91. $C_7H_{17}O_4Br_2P$. Calculated 64.77.

Preparation of the Addition Product of α, β -Dibromodiethyl Ether with Triethyl Phosphite. Triethyl phosphite, freshly distilled over sodium (b.p. 53-54° at 16 mm, n_D^{20} 1.4158), in an amount of 13 g and 18.5 g of α, β -dibromodiethyl ether, both previously cooled to -5°, were poured into the flask, which was contained in a cooling mixture. The constants were determined immediately after mixing: n_D^{20} 1.4512, d_4^{20} 1.2532.

The reaction mixture was kept cold. After 3 hours the constants were: n_D^{20} 1.4434, d_4^{20} 1.2646. Further changes in the constants are presented in Table 1, from which data it can be seen that the addition reaction is ended in 2 days.

The molecular refraction was calculated from the obtained data:

n_D^{20} 1.4462, d_4^{20} 1.3052, MR_D 81.30. $C_{10}H_{23}O_4Br_2P$. Calculated 78.05.

Preparation of the Addition Product of α, β -Dibromodiethyl Ether with Triisobutyl Phosphite. The experiment was carried out the same as described above. For reaction was taken 25 g of triisobutyl phosphite (b.p. 114-116° at 13 mm), n_D^{20} 1.4266, freshly distilled over sodium, and 23.2 g of α, β -dibromodiethyl ether. The reacting components were mixed at -3°, and the constants were determined immediately: n_D^{20} 1.4502, d_4^{20} 1.1750.

Further changes in the constants are given in Table 1, from which it follows that at room temperature the reaction is ended on the sixth day.

The molecular refraction was calculated from the obtained data:

n_D^{20} 1.4462, d_4^{20} 1.1963, MR_D 107.48. $C_{16}H_{35}O_4Br_2P$. Calculated 105.76.

Preparation of the Addition Product of α, β -Dibromodiethyl Ether with Tributyl Phosphite. For reaction was taken 25 g of tributyl phosphite (b.p. 124-126° at 15 mm, n_D^{20} 1.4318), freshly distilled over sodium and 23.2 g of α, β -dibromodiethyl ether. The mixing was done with cooling, and the constants of the mixture were determined immediately: n_D^{20} 1.4548, d_4^{20} 1.2068. Further changes in the constants are given in Table 1, from which it follows that at 17-19° the reaction is ended in 4 days.

The experiment was repeated several times. Heating, perceptible to the hand, was observed when the reactants were mixed at room temperature. When the reaction was run at 30-35° it was ended on the second day.

The molecular refraction was calculated from the obtained data:

n_D^{20} 1.4507, d_4^{20} 1.2170, MR_D 106.54. $C_{16}H_{35}O_4Br_2P$. Calculated 105.76.

Preparation of the Addition Product of α, β -Dibromodiethyl Ether with Triphenyl Phosphite. The reaction was run the same as described above. For reaction was taken 40 g of triphenyl phosphite and 30 g of α, β -dibromodiethyl ether. We were unable to follow the course of the reaction from the coefficient of refraction. We had to limit ourselves only to the determination of odor. In this case the reaction mixture acquired an orange color. The product remained liquid.

Preparation of the Addition Product of Bromomethyl n-Propyl Ether with Triethyl Phosphite. Ten grams of triethyl phosphite was placed in a ground-glass stoppered flask, to which with cooling to -10° was added 9.2 g of bromomethyl n-propyl ether. The constants were determined immediately after mixing: n_D^{20} 1.4242, d_4^{20} 1.1425.

Further observations on the reaction course were made at room temperature. The obtained data are given in Table 5.

As follows from the data in Table 5, the reaction is ended on the second day.

n_D^{20} 1.4225, d_4^{20} 1.1447, MR_D 70.94. $C_{10}H_{14}O_4BrP$. Calculated 70.29.

TABLE 5

Days	n_D^{20}	d_4^{20}
1	1.4235	1.1447
2	1.4230	1.1448
3	1.4230	1.1448
15	1.4220	1.1446

Preparation of the Methyl Ester of α -Ethoxy- β -bromoethylphosphinic Acid. In an Arbuzov flask, connected to a condenser, was placed 21 g of the addition product from α, β -dibromodiethyl ether and trimethyl phosphite. The flask was heated on the water bath. When a bath temperature of 50-60° was reached the contents of the flask began to boil with the evolution of gas. The evolved gas burns, while the insertion of a copper wire in its flame imparts a green color to it. With further heating a fraction with b.p. 75-112° was collected in an amount of 1.2 g, which was not investigated. The residue was vacuum distilled. The following fractions were obtained: 1) 45-120° (13-14 mm),

3.4 g; 2) 120-130° (13-12 mm), 0.6 g; 3) 130-140° (13-12mm), 10.5 g; residue 0.6 g.

The amount of methyl bromide formed was 4.7 g (85.1%).

The 3rd fraction after repeated distillation gave 9.2 g (60%) of colorless, quite mobile liquid:

B.p. 137° (13 mm), n_D^{20} 1.4648, d_4^{20} 1.4402, MR_D 50.08. $C_6H_{14}O_4BrP$. Calculated 49.68.

0.1707 g sub.: 38.35 ml NaOH (T 0.01850; 1 ml of solution corresponds to 0.00051205 g phosphorus). 0.1684 g sub.: 38.45 ml NaOH (the same titre). Found %: P 11.51, 11.70. $C_6H_{14}O_4BrP$. Calculated %: P 11.87.

Action of Water on the Addition Product of α, β -Dibromodiethyl Ether With Trimethyl Phosphite. The addition product (15 g) of α, β -dibromodiethyl ether was treated with 50 ml of water for 1 hour. After standing, the lower layer was separated, dried over anhydrous sodium sulfate and vacuum distilled. Two successive distillations gave 5.5 g (54%)

of the methyl ester of α -ethoxy- β -bromoethylphosphinic acid:

B.p. 137-138° (13 mm), n_D^{20} 1.4650, d_4^{20} 1.4422.

The constants are in satisfactory agreement with those for the above obtained product.

Preparation of the Ethyl Ester of α -Ethoxy- β -bromoethylphosphinic Acid. In an Arbuzov flask, fitted with condenser, was placed 30 g of the addition product from α, β -dibromodiethyl ether and triethyl phosphite; the system was connected to the vacuum. Without heating, a vacuum of 12 mm was quickly attained, but was destroyed as soon as the bath temperature was raised to 60°. The ethyl bromide was distilled at atmospheric pressure and a bath temperature of 60-80°. The amount of distilled ethyl bromide was 7 g (85.4%).

B.p. 38-39°, n_D^{20} 1.4202, d_4^{20} 1.4302.

The residue in the flask was vacuum distilled. Two successive distillations gave 16.0 g (74.1%) of colorless, quite mobile liquid:

B.p. 142-143° (10 mm), n_D^{20} 1.4570, d_4^{20} 1.3180, MR_D 59.73. $C_8H_{18}O_4BrP$. Calculated 58.91.

0.1752 g sub.: 36.05 ml NaOH (T 0.01850). 0.1808 g sub.: 36.70 ml NaOH (T 0.01850). Found %: P 10.53, 10.40. $C_8H_{18}O_4BrP$. Calculated %: P 10.72.

Action of Water on the Addition Product From α, β -Dibromodiethyl Ether and Triethyl Phosphite. The addition product (27 g) of α, β -dibromodiethyl ether with triethyl phosphite was treated with 50 ml of water with shaking for 2 hours. After separating and drying the lower layer there was obtained 19.5 g of liquid, which was first distilled at atmospheric pressure. The amount of distillate at 33-44° was 1.3°. The residue was vacuum distilled. Two successive distillations gave 10.0 g (51%) of the fraction:

B.p. 142-143° (10.5 mm), n_D^{20} 1.4555, d_4^{20} 1.3148.

This is in satisfactory agreement with the data for the earlier obtained product.

The upper water layer was distilled. A fraction (4 g) with b.p. 70-90° was obtained, which gave a positive iodoform reaction.

Preparation of the n-Butyl Ester of α -Ethoxy- β -bromoethylphosphinic Acid. The addition product of α, β -dibromodiethyl ether with tributyl phosphite was decomposed in the same manner as described above. For reaction 26 g of product was taken. At a bath temperature of 130-150° there distilled 5.8 g (81.9%) of butyl bromide:

B.p. 102-104°, n_D^{20} 1.4402, d_4^{20} 1.2742.

The residue was vacuum distilled. Two successive distillations gave 9.8 g (52.3%) of the butyl ester of α -ethoxy- β -bromoethylphosphinic acid:

B.p. 173-174° (9 mm), n_D^{20} 1.4548, d_4^{20} 1.1909, MR_D 78.61. $C_{12}H_{26}O_4BrP$. Calculated 77.38.

In a separate experiment the addition product from α, β -dibromodiethyl ether and tributyl phosphite was decomposed in vacuo. Before the start of heating the vacuum was 20 mm; under heating the vacuum was destroyed. The butyl bromide distilled at 38° (50 mm). In the remainder the results agree.

0.2254 g sub.: 39.80 ml NaOH (T 0.01850). 0.2342 g sub.: 41.20 ml NaOH (T 0.01850). Found %: P 8.99, 9.00. $C_{12}H_{26}O_4BrP$. Calculated %: P 8.98.

Action of Water on the Addition Product from α, β -Dibromodiethyl Ether and Tributyl Phosphite. The addition product (48 g) from α, β -dibromodiethyl ether and tributyl phosphite was treated with 70 ml of water with shaking. After standing, the lower layer was separated and dried over anhydrous sodium sulfate. The amount of isolated substance was 36.0 g. A small amount with a wide boiling range distilled at atmospheric pressure. The residue was vacuum distilled. Two successive distillations gave the substance:

B.p. 176-178° (13.5 mm), n_D^{20} 1.4550, d_4^{20} 1.1921.

The constants agree with the earlier obtained ester.

Preparation of the Isobutyl Ester of α -Ethoxy- β -bromoethyl phosphinic Acid. In an Arbuzov flask, fitted with condenser, was placed 25 g of the addition product from α, β -dibromodiethyl ether and triisobutyl phosphite. Boiling in the flask began at a bath temperature of 140°, while at 150-160° there distilled 5.8 g (82.3%) of isobutyl bromide:

B.p. 92-93°, n_D^{20} 1.4352, d_4^{20} 1.2632.

The residue after two successive vacuum distillations gave 9.5 g (53%) of substance:

B.p. 170-171° (14 mm), n_D^{20} 1.4523, d_4^{20} 1.1839, MR_D 78.66. $C_{12}H_{26}O_4BrP$. Calculated 77.38.

0.2026 g sub.: 36.45 ml NaOH (T 0.01850). 0.2248 g sub.: 39.00 ml NaOH (T 0.01850). Found %: P 9.19, 8.90. $C_{12}H_{26}O_4BrP$. Calculated %: P 8.98.

Action of Water on the Addition Product from α , β -Dibromodiethyl Ether and Triisobutyl Phosphite. The addition product (36 g) from α , β -dibromodiethyl ether and triisobutyl phosphite was treated with 75 ml of water with shaking. After 1 hour the lower layer was separated, dried over sodium sulfate, and vacuum distilled. Two distillations gave 8.5 g (33 %) of the fraction:

B.p. 167-168° (11 mm), n_D^{20} 1.4520, d_4^{20} 1.1848.

Action of Water on the Addition Product from Bromomethyl n-Propyl Ether and Triethyl Phosphite. The addition product (18 g) from bromomethyl n-propyl ether and triethyl phosphite was treated with 50 ml of water with shaking. After 3 hours the lower layer was separated, dried over sodium sulfate, and vacuum distilled. The following fractions were obtained: 1) to 110° (25 to 15 mm), 2 g; 2) 110-122° (15-13 mm), 1.5 g; 3) 122-125° (10 mm), 6.2 g.

Redistillation of the 3rd fraction gave 5 g (42.4%) of the product:

B.p. 122-123° (9 mm), n_D^{20} 1.4260, d_4^{20} 1.0371, MR_D 51.88. $C_6H_{13}O_4P$. Calculated 51.15.

The constants are in satisfactory agreement with the earlier obtained ethyl ester of propoxymethylphosphinic acid [16].

Preparation of the Methyl Ester of α -Ethoxyvinylphosphinic Acid. In a flask, fitted with mechanical stirrer, reflux condenser and dropping funnel, was placed 100 ml of a 2% anhydrous alcohol solution of potassium hydroxide. To it with stirring and ice cooling was slowly added 9 g of the methyl ester of α -ethoxy- β -bromomethylphosphinic acid. After all of the ester had been added the reaction mixture was brought to the boil. The precipitate of potassium bromide was filtered and washed with a small portion of anhydrous alcohol. The alcohol was distilled off and the residue was vacuum distilled. Two successive distillations gave 4.7 g (75.3%) of the methyl ester of α -ethoxyvinylphosphinic acid as a colorless, quite mobile liquid with characteristic odor. Turns yellow in the air.

B.p. 122-123° (10 mm), n_D^{20} 1.4462, d_4^{20} 1.1702, MR_D 41.05. $C_6H_{13}O_4PF$. Calculated 41.44.

0.1234 g sub.: 41.20 ml NaOH (T 0.01850). 0.1315 g sub.: 40.80 ml NaOH (T 0.01850). Found %: P 17.10, 16.92. $C_6H_{13}O_4P$. Calculated %: P 17.22.

Preparation of the Ethyl Ester of α -Ethoxyvinylphosphinic Acid. The ethyl ester of α -ethoxyvinylphosphinic acid was prepared in the same manner as described above. To a solution of 5 g of potassium hydroxide in 300 ml of anhydrous alcohol with stirring and cooling was added 25.5 g of the ethyl ester of α -ethoxy- β -bromoethylphosphinic acid. After conclusion of reaction the potassium bromide was filtered, the alcohol distilled, and the residue vacuum distilled. There was obtained 14.9 g (76.6 %) of colorless liquid with characteristic odor:

B.p. 128-130° (10 mm), n_D^{20} 1.4408, d_4^{20} 1.0930. MR_D 50.21. $C_8H_{17}O_4PF$. Calculated 50.67.

0.1958 g sub.: 56.50 ml NaOH (T 0.01850). 0.1734 g sub.: 49.90 ml NaOH (T 0.01850). Found %: P 14.80, 14.65. $C_8H_{17}O_4P$. Calculated %: P 14.90.

Preparation of the n-Butyl Ester of α -Ethoxyvinylphosphinic Acid. To a solution of 3 g of potassium hydroxide in 150 ml of anhydrous alcohol with stirring and cooling was added 18 g of the n-butyl ester of α -ethoxy- β -bromoethylphosphinic acid. After filtering off the potassium bromide and distilling off the alcohol the residue was vacuum-distilled. There was obtained 10.8 g (79.1 %) of the n-butyl ester of α -ethoxyvinylphosphinic acid as a liquid with characteristic odor, turning yellow in the air:

B.p. 164-166° (13 mm), n_D^{20} 1.4426, d_4^{20} 1.0182. MR_D 68.75. $C_{12}H_{26}O_4PF$. Calculated 69.15.

0.2186 g sub.: 48.65 ml NaOH (T 0.01850). 0.2040 g sub.: 45.80 ml NaOH (T 0.01850). Found %: P 11.40, 11.51. $C_{12}H_{26}O_4P$. Calculated %: P 11.74.

Preparation of the Isobutyl Ester of α -Ethoxyvinylphosphinic Acid. To a solution of 2.6 g of potassium hydroxide in 150 ml of anhydrous alcohol with stirring and cooling was added 13 g of the isobutyl ester of α -ethoxy- β -bromoethylphosphinic acid. After removal of the potassium bromide and distilling off the alcohol the residue was vacuum-distilled. There was obtained 7.5 g (77.2 %) of the isobutyl ester of α -ethoxyvinylphosphinic acid:

B.p. 148-149° (10 mm), n_D^{20} 1.4378, d_4^{20} 0.9954, MR_D 69.44. $C_{12}H_{26}O_4P$. Calculated 69.15.

0.1918 g sub.: 42.85 ml NaOH (T 0.01850). Found %: P 11.45. $C_{12}H_{25}O_4P$. Calculated %: P 11.74.

SUMMARY

1. It was shown that the reaction of α - β -dibromodiethyl ether with esters of phosphorous acid gives addition products.
2. It was shown that heating of the addition products obtained from α , β -dibromodiethyl ether and phosphites results in the cleavage of alkyl halide and the esters of α -ethoxy- β -bromoethylphosphinic acid are formed. The same esters are obtained by the action of water on the addition products.
3. As a result, it was shown that the Arbuzov reaction for the rearrangement of phosphites, obtained from aliphatic alcohols, can be run in two separate independent stages. In this way it was shown that the scheme proposed by A. E. Arbuzov remains the general scheme for this reaction.
4. It was shown that the cleavage of hydrogen bromide from the esters of α -ethoxy- β -bromoethylphosphinic acid results in the formation of the esters of α -ethoxyvinylphosphinic acid.

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OXIDATION OF ESTERS OF 9-OCTADECENOIC ACIDS

N. P. Bulatsky

We had communicated earlier [1] that the geometric isomers of 9-octadecenoic acid are oxidized at a different rate by potassium permanganate in acetone solution.

At the suggestion of A. K. Plisov this observation was transferred to the oxidation of the methyl, ethyl, propyl and butyl esters of oleic and elaidic acids for the purpose of elucidating the influence of the alcohol radical structure and the dependence of reactivity on the spatial configuration of the molecule.

The performed studies revealed that the oxidation rate depends on both the spatial configuration of the molecule and the structure of the alcohol radicals entering into the composition of the ester.

EXPERIMENTAL

The esters of oleic and elaidic acids were obtained by the esterification of the acids with the anhydrous alcohol in the presence of sulfuric acid [2]. The properties of the obtained esters are given in Table 1.

TABLE 1

Ester	Boiling point at the pressure (in mm)	Saponification Number	Iodine Number (by Hubel)
Methyl oleate	178° (5)	190	85.93
Ethyl oleate	182 (5)	180.3	81.29
Propyl oleate	184.5 (5)	171.9	78.39
Butyl oleate	194 (5)	166.0	73.88
Methyl elaidate	178.4 (5)	188.6	84.96
Ethyl elaidate	183 (5)	181.2	82.30
Propyl elaidate	186 (5)	172.4	77.64
Butyl elaidate	196 (5)	166.2	73.62

TABLE 2

Experimental Temperature 20°; Concentration of Oxidized Esters 0.0442 N.; Concentration of Oxidizing Agent 0.0410 N.

Time of oxidation (min.)	Amount of Thiosulfate (in ml)							
	Methyl oleate	Ethyl oleate	Propyl oleate	Butyl oleate	Methyl elaidate	Ethyl elaidate	Propyl elaidate	Butyl elaidate
15	6.64	6.72	6.81	7.00	7.42	7.54	7.63	7.61
30	5.38	5.48	5.72	5.81	6.73	6.78	6.82	6.91
45	4.49	4.58	4.69	4.97	5.96	6.03	6.06	6.12
60	3.74	3.83	3.85	4.09	5.28	5.26	5.53	5.58
75	2.92	3.20	3.30	3.37	4.60	4.66	4.60	4.68
90	2.35	2.49	2.52	2.68	3.68	3.78	3.92	3.98

The oxidation studies were made in the same way as is described in detail in the experiments with the free acids [1].

The results of the experiments, run at different temperatures and different concentrations of esters and oxidizing agent, are given in Tables 2-4.

TABLE 3

Experimental Temperature 10°; Concentration of Oxidized Esters 0.0442 N.; Concentration of Oxidizing Agent 0.0410 N.

Time of oxidation (min.)	Amount of Thiosulfate (in ml)							
	Methyl oleate	Ethyl oleate	Propyl oleate	Butyl oleate	Methyl elaidate	Ethyl elaidate	Propyl elaidate	Butyl elaidate
30	6.86	6.82	6.99	7.14	7.55	7.61	7.78	7.83
60	5.56	5.65	5.97	5.93	6.84	7.02	7.10	7.12
90	4.63	4.78	4.96	5.11	6.16	6.39	6.55	6.56
120	3.95	3.97	4.10	4.27	5.60	5.75	5.90	5.98
150	3.14	3.35	3.51	3.57	4.96	5.20	5.30	5.42
180	2.32	2.53	2.78	2.82	4.22	4.60	4.67	4.78

TABLE 4

Experimental Temperature 20°; Concentration of Oxidized Esters 0.0221 N.; Concentration of Oxidizing Agent 0.0451 N.

Time of oxidation (min.)	Amount of Thiosulfate (in ml)							
	Methyl oleate	Ethyl oleate	Propyl oleate	Butyl oleate	Methyl elaidate	Ethyl elaidate	Propyl elaidate	Butyl elaidate
15	8.84	8.76	8.92	8.95	9.35	9.30	9.42	9.50
30	7.95	8.08	8.20	8.18	8.60	8.74	8.80	8.78
45	7.39	7.47	7.50	7.52	8.08	8.02	8.16	8.15
60	6.75	6.80	6.94	7.10	7.54	7.41	7.49	7.62
75	6.49	6.56	6.52	6.68	6.94	7.08	7.12	7.12
90	5.99	6.04	6.14	6.18	6.54	6.68	6.68	6.70

The obtained data (Tables 2-4) indicate that the esters of oleic (cis-) acid are more rapidly oxidized with potassium permanganate in acetone solution than are the corresponding esters of elaidic (trans-) acid.

From the data in Tables 2-4 it can be seen that in measure with increase in the alcohol radical (from methyl to butyl) that the oxidation rate of the esters of both oleic and elaidic acids is diminished.

SUMMARY

1. The esters of oleic acid are more rapidly oxidized with potassium permanganate in acetone solution than are the esters of elaidic acid.
2. An increase in the size of the alcohol radical in the ester molecule leads to a reduction in the oxidation rate.

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* Consultants Bureau Translation, p. 1845.

OXIDATION OF VINYLACETYLENE HYDROCARBONS WITH ORGANIC HYDROPEROXIDES

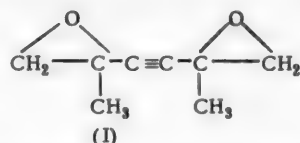
III. OXIDATION OF 3,6-DIMETHYL-2,6-OCTADIEN-4-YNE WITH ACETYL HYDROPEROXIDE (PEROXYACETIC ACID)

N. M. Malenok and S. D. Kul'kina

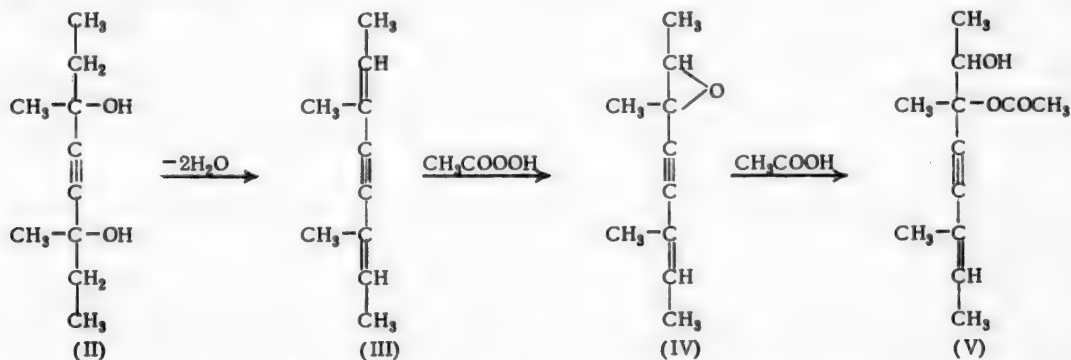
In previous papers [1] we communicated the results obtained by us on the oxidation of vinylacetylene hydrocarbons of diverse structure with acetyl hydroperoxide (peroxyacetic acid).

In the present paper we oxidized the divinylacetylene hydrocarbons with peroxyacetic acid for the purpose of obtaining their first product – the acetylene diepoxide and studying its properties.

The reason for this was the fact that the acetylene diepoxides have been studied but slightly. In this field are known the investigations of Gershtein [2], who in the reaction of the acetylene dichlorohydrin dichlorotetramethylbutynediol with powdered KOH obtained two stereoisomers of the acetylene diepoxide:



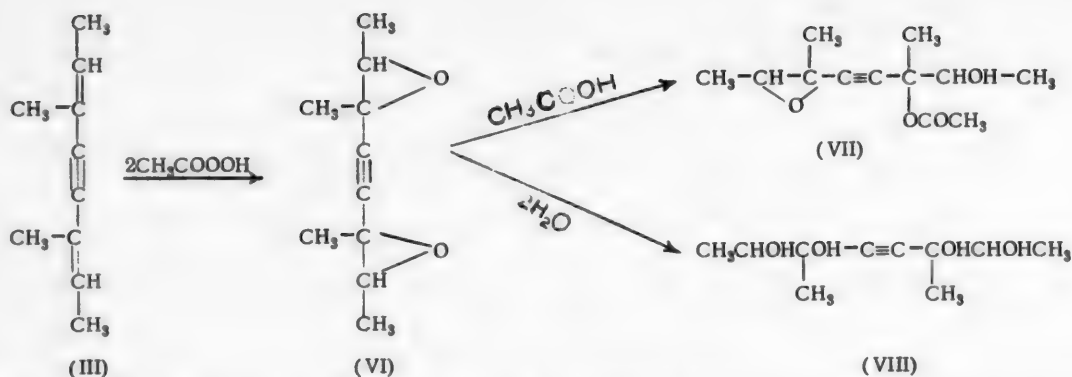
The hydrolysis of these diepoxides gave acetylene erythritols, in which the presence of hydroxyl groups was demonstrated by preparing the tetraacetyl derivatives. For obtaining the divinylacetylene hydrocarbon – 3,6-dimethyl-2,6-octadien-4-yne (III) – we first synthesized from methyl ethyl ketone and acetylene glycol by the method of Zh. I. Iotsich the compound 3,6-dimethyl-4-octyn-3,6-diol (II), which was dehydrated with 40% H_2SO_4 to the unsaturated hydrocarbon (III). Its oxidation with one mole of peroxyacetic acid gave the vinylacetylene alcohol acetate – 3,6-dimethyl-3-acetoxy-6-octen-4-yn-2-ol (V), which proves to be a secondary product, formed from the vinylacetylene monoepoxide (IV) and acetic acid; in this connection the acetylene diepoxide – 3,6-dimethyl-2,3,6,7-diepoxy-4-octyne (VI) was also isolated.



The oxidation of 3,6-dimethyl-2,6-octadien-4-yne with two moles of peroxyacetic acid gave the same acetylene diepoxide that was obtained in the first case (VI) and also the monoepoxide – 3,6-dimethyl-6-acetoxy-2,3-epoxy-4-octyn-7-ol (VII), which was formed by the reaction of the diepoxide with acetic acid.

The diepoxide was subjected to hydrolysis; the result was the acetylene erythritol – 3,6-dimethyl-4-octyn-2,3,6,7-tetrol (VIII).

The oxidation of the hydrocarbon (III) with 4 moles of peroxyacetic acid, calculated on the basis of oxidizing two double bonds and one triple bond, gave the same monoepoxide (VII) as was obtained in the previous case.



The presence of a triple bond in this substance and in the erythritol was demonstrated by quantitative bromination. As a result, in the oxidation of divinylacetylene hydrocarbons with peroxyacetic acid the oxidation proceeds at the double bonds, while the triple bond remains untouched.

We observed a similar phenomenon also in the oxidation of vinylacetylene hydrocarbons with peroxyacetic acid in which the hydrogens at the carbon atoms of the triple bond were substituted by hydrocarbon radicals [3].

EXPERIMENTAL

Oxidation of 3,6-Dimethyl-2,6-octadien-4-yne with Peroxyacetic Acid Calculated on the Basis of 2 Moles of Peroxyacetic Acid for 1 Mole of Hydrocarbon

The divinylacetylene hydrocarbon (57.5 g) (b.p. 71-73°, 20 mm) was oxidized in anhydrous diethyl ether with 173 g of 38% peroxyacetic acid at -8°. The reaction ran with elevation of the temperature to -5°. After all of the peroxyacetic acid had been added to the hydrocarbon the reaction mixture was let stand at room temperature.

Together with the oxidation of the divinylacetylene hydrocarbon by peroxyacetic acid a control was run under similar conditions.

The oxidation progress for both the basic and control experiments was determined daily by titration with 0.1 N $\text{Na}_2\text{S}_2\text{O}_3$ solution. For this 20 ml aliquots of the experimental and control solutions that had been previously diluted 100-fold with water were taken and the amount of unreacted peroxyacetic acid determined iodometrically. The results are given in Table 1.

TABLE 1

Nature of Experiment	Milliliters of 0.1 N $\text{Na}_2\text{S}_2\text{O}_3$ consumed for titration of unreacted peroxyacetic acid after number of days:							
	1	2	3	4	5	6	7	8
Basic	7.45	1.0	0.7	0.45	0.3	0.2	0.15	0.15
Control	7.45	7.45	7.45	7.45	7.4	7.4	7.4	7.4

From the data in Table 1 it can be seen that the oxidation of 3,6-dimethyl-2,6-octadien-4-yne with peroxyacetic acid proceeded for seven days. In this length of time the control showed a very small change in the peroxyacetic acid concentration.

After 7 days the reaction mixture was washed with water, and then with soda. The ether layer was separated, dried for a day over potash, and then filtered. The ether was distilled off, and from the residual mass a 3-fold fractional distillation gave two substances: 1) b.p. 62-64° (0.5 mm), 4.2 g; 2) b.p. 121-122° (1 mm), 16.4 g.

Investigation of the Substance with B.P. 62-64° (0.5 mm). Lachrymatory liquid with a light yellow color. Soluble in diethyl ether, ethyl alcohol and chloroform, insoluble in water.

d_{40}^{20} 0.9630, n_D^{20} 1.4587, M_R 47.09; calculated 46.66.

0.1294 g sub.: 0.3483 g CO_2 ; 0.1001 g H_2O . 0.1055 g sub.: 0.2833 g CO_2 ; 0.0820 g H_2O . 0.2303 g sub.: 23.03 g benzene: Δt 0.332°. Found %: C 73.41, 73.24; H 8.65, 8.69. M 155.6. $\text{C}_{10}\text{H}_{14}\text{O}_2$. Calculated %: C 72.29; H 8.43. M 166.

In acid medium the obtained diepoxide - 3,6-dimethyl-2,3,6,7-diepoxy-4-octyne (VI) - liberates iodine from potassium iodide and fails to show the presence of active hydrogen with methylmagnesium iodide.

The high content of carbon in the diepoxide when compared to theory is, apparently, due to some impurity, which is removed only with difficulty.

Investigation of the Substance with B.P. 121-122° (1 mm). The viscous liquid is soluble in the same solvents as the diepoxide; in soluble in water.

d_{20}^{20} 1.0585, n_D^{20} 1.4671, MR_D 59.01; calculated 58.94.

0.1259 g sub.: 0.2956 g CO₂; 0.0957 g H₂O. 0.1287 g sub.: 0.2998 g CO₂; 0.0958 g H₂O. 0.2588 g sub.: 22.9 g benzene: Δt 0.251°. 0.2624 g sub.: 27.9 ml CH₄ (15°, 744 mm). Found %: C 64.02, 63.53; H 8.42, 8.27; OH 7.54, M 230.9. C₁₂H₁₈O₄. Calculated %: C 63.72; H 7.98; OH 7.52. M 226.

Hydrolysis of the Diepoxide - 3,6-Dimethyl-2,3,6,7-diepoxy-4-octyne. Two grams of the diepoxide was heated on the water bath to 60° with 15 ml of water in the presence of HCl traces for 2 hours. The result was a solution with a small amount of tarry residue. After removing the tar the liquid was evaporated on the water bath. A crystalline substance was obtained, insoluble in ether, benzene and chloroform, and readily soluble in ethyl alcohol and water. After repeated washing with diethyl ether there was obtained 1.4 g of crystals with m.p. 134-136°.

0.1194 g sub.: 0.2589 CO₂; 0.0943 g H₂O. 0.1126 g. sub.: 0.2449 g CO₂; 0.0946 g H₂O. 0.2015 g sub.: 16.58 g H₂O; Δt 0.114°. Found %: C 59.14, 59.32; H 8.84, 9.38. M 198.5. C₁₀H₁₈O₄. Calculated %: C 59.41; H 8.98. M 202.

The analysis data show that the crystalline substance is the acetylene erythritol-3,6-dimethyl-4-octyn-2,3,6,7-tetrol.

We were unable to determine the number of hydroxyl groups in it due to its insolubility in isoamyl ether and anisole.

The presence of a triple bond in the acetylene erythritol was shown by quantitative bromination.

0.2010 g of substance, dissolved in water, added 0.3345 g of bromine, which corresponds to theory for the addition of 4 atoms of bromine or 0.3184 g for 1 triple bond.

Oxidation of 3,6-Dimethyl-2,6-octadien-4-yne with Peroxyacetic Acid Calculated on the Basis of 1 Mole of Peroxyacetic Acid for 1 Mole of Hydrocarbon

The divinylacetylene hydrocarbon (33 g) was oxidized in anhydrous diethyl ether with 50 g of 38% peroxyacetic acid at -5°. The reaction proceeded with elevation of the temperature to 0° and was completed on the third day, which can be seen from Table 2.

TABLE 2

Nature of Experiment	Milliliters of 0.1 N Na ₂ S ₂ O ₃ consumed for titration of unreacted peroxyacetic acid after number of days:			
	1	2	3	4
Basic	5.65	0.25	0.05	0.05
Control	5.65	5.65	5.65	5.65

The control was run under the same conditions as the experiment and for four days failed to show a change in the peroxyacetic acid concentration.

The diethyl ether, formed acetic acid and unreacted peroxyacetic acid were separated from the oxidation products the same as in the previous case. From the residual mass a 3-fold fractional distillation gave two substances: 1) b.p. 62-64° (0.5 mm), 2.5 g, which proved to be the diepoxide - 3,6-dimethyl-2,3,6,7-diepoxy-4-octyne (VI), and 2) b.p. 95-96° (0.5 mm), 6 g.

Investigation of the Substance with B.P. 95-96° (0.5 mm). Soluble in diethyl ether, chloroform and acetone, insoluble in water.

d_{20}^{20} 0.9936, n_D^{20} 1.4779, MR_D 59.81; calculated 58.33.

0.1304 g sub.: 0.3295 g CO₂; 0.1030 g H₂O. 0.1141 g sub.: 0.2863 g CO₂; 0.0930 g H₂O. 0.1994 g sub.: 23.99 g benzene: Δt 0.206°; 0.1226 g sub.: 15.85 ml CH₄ (15°, 751 mm). Found %: C 68.91, 68.43; H 8.77, 9.06; OH 9.53. M 207.4. C₁₂H₁₈O₃. Calculated %: C 68.57; H 8.57; OH 8.10. M 210.

The investigated substance is the vinylacetylene alcohol acetate - 3,6-dimethyl-3-acetoxy-6-octen-4-yn-2-ol (V).

Oxidation of 3,6-Dimethyl-2,6-octadien-4-yne with Peroxyacetic Acid Calculated on the Basis of 4 Moles of Peroxyacetic Acid for 1 Mole of Hydrocarbon

The divinylacetylene hydrocarbon (21 g) was oxidized with 160 g of peroxyacetic acid under the same conditions as in the previous cases. The result was the isolation of only one substance with b.p. 121-122° (1mm) in amount of 7.6 g, which on investigation proved to be the monoepoxide - 3,6-dimethyl-6-acetoxy-2,3-epoxy-4-octyn-7-ol (VII), obtained by us earlier.

The presence of a triple bond in this substance was determined by quantitative bromination.

0.3785 g of substance, dissolved in chloroform, added 0.4676 g of bromine. The calculated theory should have resulted in the addition of 0.5360 g of bromine for 1 triple bond.

The low amount of bromine added to the substance, when compared to theory, can be explained by slight evaporation of the solvent - chloroform - under prolonged bromination (6 hours).

SUMMARY

1. The oxidation of 3,6-dimethyl-2,6-octadien-4-yne with one mole of peroxyacetic acid gave the vinylacetylene alcohol acetate - 3,6-dimethyl-3-acetoxy-6-octen-4-yn-2-ol and the diepoxide, the hydrolysis of which gave the acetylene erythritol - 3,6-dimethyl-4-octyn-2,3,6,7-tetrol.

2. The oxidation of 3,6-dimethyl-2,6-octadien-4-yne with two moles of peroxyacetic acid gave the acetylene diepoxide and the monoepoxide - 3,6-dimethyl-6-acetoxy-2,3-epoxy-4-octyn-7-ol, which is also formed when the hydrocarbon is oxidized with 4 moles of peroxyacetic acid.

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Minsk Institute of Medicine

* Consultants Bureau Translation, p. 1181.

** Consultants Bureau Translation, p. a-151.

UNSATURATED CYCLIC HYDROCARBONS AND THEIR HALOGEN DERIVATIVES

XVI. ACTION OF METALLIC SODIUM ON 2,3-DIBROMO-1,3-CYCLOHEXADIENE

N. A. Domnin, G. K. Krasilnikova and V. A. Cherkasova

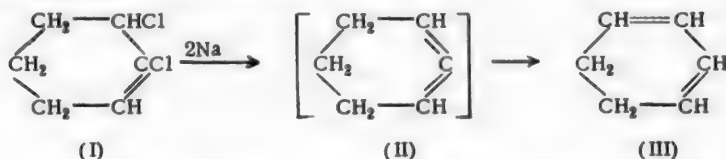
It had already been shown earlier by one of us [1] that in the action of metallic sodium or zinc dust on 1,2-dichloro-2-cyclohexene (I) the expected isomer of the originating 1,2-cyclohexadiene, namely 1,3-cyclohexadiene, is not formed at all; here it was shown by us that the reaction proceeds only by way of polymerization, the mechanism of which remains obscure.

The problem remained unsolved as to the main reason for making it impossible for the isomerization reaction to proceed in the direction of forming the monomeric products.

As a result of reaction with metallic sodium the polymeric products are completely devoid of chlorine, which means that the 1,2-dichloro-2-cyclohexene (I) completely releases all of its chlorine to the metallic sodium.

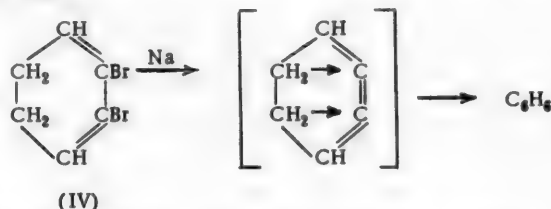
It was shown by D. V. Tishchenko [2] that the formation of 1,2-cyclohexadiene (II) as an intermediate reaction product takes place in the action of quinoline on 1,2,2-trichlorocyclohexane, as a result of which 1-chloro-1,3-cyclohexadiene is formed.

If for our case it is assumed that as intermediate product the short-lived 1,2-cyclohexadiene (II) is formed, then according to generally established opinion [3] it should easily suffer isomerization through the shifting of one hydrogen atom in the beta-position to 1,3-cyclohexadiene (III).

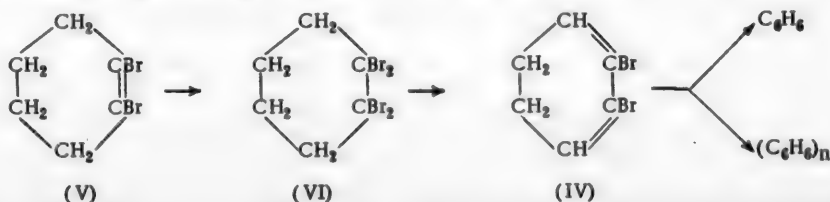


Since the reaction completely fails to proceed in this reaction, then it must be assumed that hydrogen shifting fails to occur here.

The question relative to the difficulty or ease of hydrogen shifting in general up to now remains slightly developed with respect to unsaturated cyclic and bicyclic hydrocarbons; consequently, it appeared of interest to us to attempt the introduction of even some clarity into the picture. For the realization of this attempt we started from the compound, which, in the creation of cumulative double bonds in its molecule, could easily be isomerized into the stable monomeric form — the benzene ring



It was proposed to conduct the investigation in accord with the following scheme:



The structure of the starting 1,2-dibromo-1-cyclohexene (V) was shown by Favorsky and Bozhovsky [4]; the structure of the 1,1,2,2-tetrabromocyclohexane (VI) was shown by us via the fact that in the action of zinc dust on it two bromine atoms are split off and the starting 1,2-dibromo-1-cyclohexene (V) is obtained.

The structure of the 2,3-dibromo-1,3-cyclohexadiene (IV) was demonstrated by its oxidation with potassium permanganate to succinic and oxalic acids.

As a result of the performed work it was shown that in the action of zinc dust on 2,3-dibromo-1,3-cyclohexadiene (IV) the compound fails to release its bromine atoms to the zinc; metallic sodium removes both of the bromine atoms from 2,3-dibromo-1,3-cyclohexadiene (IV) but as a result of this reaction only a polymeric product is formed.

EXPERIMENTAL

1,2-Dibromo-1-cyclohexene was synthesized by the earlier described method [4].

Preparation of 1,1,2,2-Tetrabromocyclohexane. To 20 g of 1,2-dibromo-1-cyclohexene in chloroform (1:1) was added with cooling 4.2 ml (13.4 g) of bromine in chloroform (1:1), and the mixture was allowed to stand for a day at room temperature. Then the mixture was heated for an hour at 30-40° and to the heated mixture was added 1-1.5 ml of distilled water. Slight evolution of hydrogen bromide was observed, but the mixture failed to decolorize; for that reason it was let stand for another day at room temperature, and then it was again heated to 30-40°. The unreacted bromine was removed by washing with dilute sodium sulfite solution, and the treated solution was washed with water and dried over calcium chloride. The solvent was removed with an oil pump into a trap, immersed in a cooling mixture of dry ice and ether. The residue was distilled at 10 mm. The fraction collected in the range 100-112° crystallized completely and proved to be the starting 1,2-dibromo-1-cyclohexene. With further elevation of the temperature the residue in the flask began to decompose. With ordinary cooling of the flask the residue crystallized completely. The crystalline mass was extracted with ether from the flask, poured into a crystallizing dish and after removal of the ether it again crystallized. The crystals, pressed on porous plate, melted at 188-190°, with slight decomposition and on standing partially evolved hydrogen bromide and bromine.

After recrystallization from ethyl alcohol stable colorless crystals with m.p. 209° were obtained. From 20 g of the dibromide there was obtained 8.2 g of pure crystalline 1,1,2,2-tetrabromocyclohexane.

0.2629 g sub.: 17.4 g benzene: Δt 0.191°. 0.2456 g sub.: 15.03 g benzene: Δt 0.21°. Found: M 394.3, 396. $C_6H_8Br_4$. Calculated: M 400.

0.1388 g sub.: 0.2608 g AgBr. 0.1124 g sub.: 0.2119 g AgBr. Found %: Br 79.90, 80.24. $C_6H_8Br_4$. Calculated %: Br 79.90.

To determine its structure the 1,1,2,2-tetrabromocyclohexane was treated with zinc dust in boiling dioxane. In this way an almost quantitative yield of the starting 1,2-dibromo-1-cyclohexene was obtained, the mixed melting point of which with authentic 1,2-dibromo-1-cyclohexene was 39-40° and failed to show a depression.

Cleavage of Hydrogen Bromide from 1,1,2,2-Tetrabromocyclohexane. The crystalline tetrabromide was added to a boiling 20% alcohol solution of potassium hydroxide, which was taken in excess (30%). The mixture was heated on the water bath for 4 hours, and after cooling was diluted with water to complete solution of the precipitated potassium bromide. The formed dibromide separated as an oil on the bottom of the flask. The oil was separated, dissolved in ether, the solution washed several times with water, and dried over calcium chloride. After distilling off the ether the residue was distilled at 25 mm; 20 g of a fraction with b.p. 116-117° was collected.

d_4^{20} 1.8490, n_D^{20} 1.5701, M_R^{20} 42.23. $C_6H_8Br_2$. Calculated 42.00.

0.2973 g sub.: 12.51 g benzene: Δt 0.52°. 0.2343 g sub.: 12.25 g benzene: Δt 0.36°. Found M 235, 234. $C_6H_8Br_2$. Calculated: M 238.

0.1196 g sub.: 0.1882 g AgBr. 0.1074 g sub.: 0.1687 g AgBr. Found %: Br 66.91, 66.86. $C_6H_8Br_2$. Calculated %: Br 67.92.

Determination of the Structure of the Dibromide. The dibromide was oxidized with potassium permanganate, taken in an amount equivalent to 6 oxygen atoms for 1 mole of the dibromide.

To 6 g of the dibromide was added in small portions 15.8 g of potassium permanganate, first as a saturated solution and then as a powder. The mixture was constantly cooled and shaken. On conclusion of oxidation the mixture was heated on the water bath to coagulate the manganese dioxide. The precipitate was filtered and washed with hot water. The filtrate was made slightly alkaline by the addition of potassium hydroxide; steam distillation failed to disclose any

neutral products. The filtrate was evaporated, acidified with sulfuric acid, and extracted with diethyl ether for 2 days.

The yield of crystalline acid was 1.2 g, which after recrystallization from water and drying melted at 182.5-183°. The mixed melting point of this acid with authentic succinic acid failed to be depressed.

0.1140 g sub.: 19.2 ml 0.1 N NaOH. 0.1215 g sub.: 20.5 ml 0.1 N NaOH. Found equiv. 59.20, 59.11. $C_4H_6O_4$. Calculated: equiv. 59.00.

0.1567 g salts: 0.1008 g Ag. Found %: Ag 64.43. $C_4H_4O_4Ag_2$. Calculated %: Ag 65.03.

The dibromide fails to condense with maleic anhydride.

Cleavage of Bromine from 2,3-Dibromo-1,3-cyclohexadiene. In a thick-walled tube was placed 7 g of freshly-cut metallic sodium in 20 ml of anhydrous dioxane. The end of the tube was tightly closed with a stopper with calcium chloride tube. After complete cessation of hydrogen bubble evolution there was introduced into the tube 10 g of 2,3-dibromo-1,3-cyclohexadiene; after this the tube was sealed and let stand at room temperature until reaction was complete.

The reaction of metallic sodium with the dibromide began immediately. The sodium pieces began to blacken on the corners and edges, and then the whole mixture turned dark. After two days the tube was opened, the solution decanted from the sodium bromide precipitate and remaining metallic sodium, while the residue was washed several times with dioxane. The solution was filtered to remove turbidity and then diluted with water; here a weakly stable emulsion was formed and on the walls of the separatory funnel there deposited yellow flocs of polymerization products. We failed to disclose the presence of even traces of any monomers or the expected benzene. In the reaction tube in measure with dioxane removal there also separated a light yellow mass of polymerization products. They were extracted with ether, boiled with distilled water, and then dried. About 2 g of the pure polymers was obtained. The hard amorphous substance is readily soluble in ether, benzene and dioxane. The qualitative test for halogen was negative.

0.1347 g sub.: 16.56 g benzene: Δt 0.14°. 0.2215 g sub.: 11.03 g benzene: Δt 0.33°. Found M 297, 312. $(C_6H_6)_4$. Calculated: M 320.

The elementary analysis of the polymer for carbon and hydrogen failed to give consistent results, since the polymer burns only with great difficulty.

SUMMARY

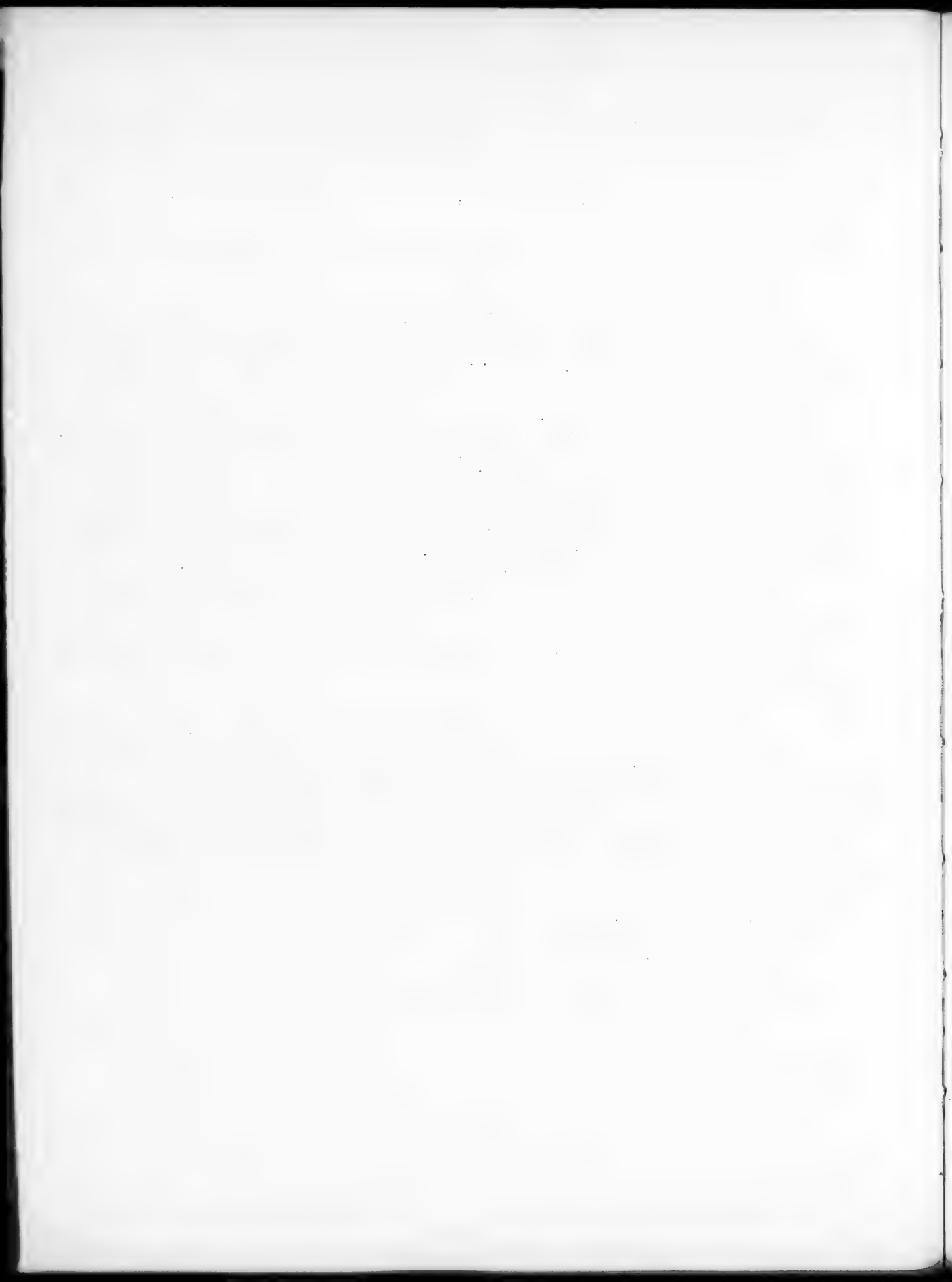
1. A full characterization was given and the structure of 2,3-dibromo-1,3-cyclohexadiene was proven.
2. It was shown that the action of metallic sodium on 2,3-dibromo-1,3-cyclohexadiene completely fails to give any of the theoretically possible benzene, but instead only polymerization products are formed.
3. The present work raised some new questions on the mechanism of polymerization, on the ease or difficulty of shifting hydrogen atoms in different cases, on the stability of different types of deformed molecules, on the impossibility of their temporary origin, etc.

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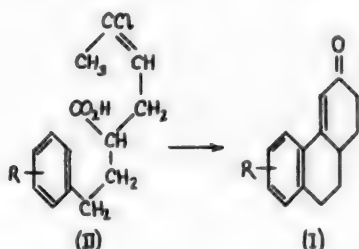


SYNTHESIS OF POLYCYCLIC HYDROAROMATIC KETONES

VIII. 8-METHYL- AND 8-METHOXY-3-KETO-1,2,3,9,10,10a-HEXAHYDROPHENANTHRENES

G. T. Tatevosyan and A. G. Vardanyan

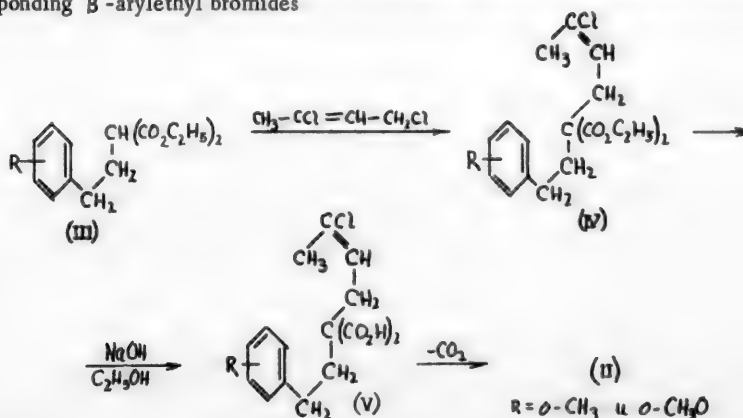
In previous communications it was shown that the yields of substituted 3-keto-1,2,3,9,10,10a-hexahydrophenanthrenes (I), formed in the reaction of α -(3-chlorocrotyl)- γ -phenylbutyric acids (II) with sulfuric acid, are influenced by the presence of methyl and methoxy groups in the meta- and para-positions of the aromatic ring



It was found that the methyl group, irrespective of whether it is found in the meta- or para-position with respect to the side chain (II, R = *m*- or *p*-CH₃), fails to exert any marked influence on the yield of the corresponding tricyclic ketone [1], while at the same time the position of the methoxyl group strongly influences the course of the studied conversion [2]. Whereas the methoxyl group found in the meta-position (II, R = *m*-CH₃O), not changing the basic course of the reaction, only slightly lowers the yield of tricyclic ketone (I, R = 7-CH₃O), which, apparently, is explained by the comparative ease with which the methoxylated aromatic ring is sulfonated, the same group in the para-position (II, R = *p*-CH₃O) completely excludes the possibility of a one-step realization of this transformation; the starting acid, similar to the γ -phenylbutyric acid not substituted in the side chain [3], when treated with sulfuric acid is practically completely sulfonated. This result can be explained as being due to the ease with which the methoxylated ring sulfonates and also to the circumstance that the methoxyl group, being strongly ortho-, para-orienting, prevents the intramolecular acylation that should take place at the meta-position with respect to this group.

For the purpose of obtaining the complete picture on the influence of alkyl (for example methyl) and alkoxy (for example methoxyl) groups on the yields of 3-keto-hexahydrophenanthrenes obtained by the indicated method a study was made of the analogous conversion of α -(3-chlorocrotyl)- γ -phenylbutyric acids in which the same substituents were contained in the ortho-position of the aromatic ring (II, R = *o*-CH₃ and *o*-CH₃O).

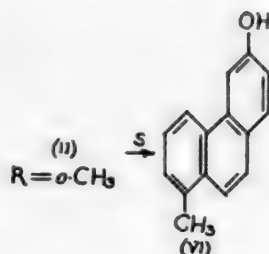
The starting acids (II, R = *o*-CH₃ and *o*-CH₃O) were obtained via the malonic ester synthesis from 1,3-dichloro-2-butene and the corresponding β -arylethyl bromides



The reaction of α -(3-chlorocrotyl)- γ -(*o*-tolyl)butyric acid (II, R = *o*-CH₃) with sulfuric acid (d 1.78) at 60-75° gave 3-keto-8-methyl-1,2,3,9,10,10a-hexahydrophenanthrene (I, R = 8-CH₃). The yield of this ketone (62.95%) was of the same order as the yields of the unsubstituted ketone and its two other methyl homologs [1].

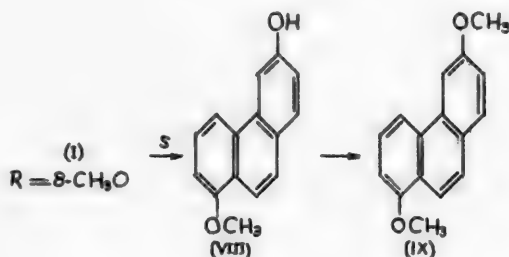
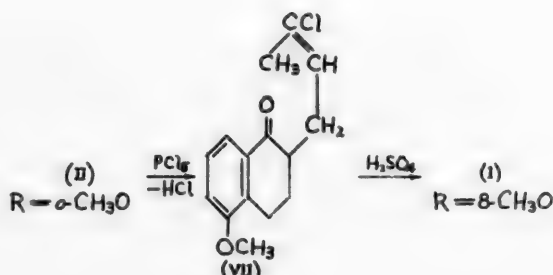
The dehydrogenation of the ketone with sulfur gave 3-hydroxy-8-methylphenanthrene (VI).

α -(3-Chlorocrotyl)- γ -(*o*-anisyl)butyric acid (II, R = *o*-CH₃O), similar to its *p*-anisyl isomer, is completely sulfonated under the influence of sulfuric acid. In this case also the tricyclic methoxy ketone (I, R = 8-CH₃O) can be obtained only in a circuitous manner, consisting in the thermal dehydrochlorination of the acid chloride of the acid (II, R = *o*-CH₃O), subsequent hydrolysis, and intramolecular aldol condensation of the substituted tetralone (VII) under mild conditions, not favorable to sulfonation.



The structure of the methoxy ketone (I, R = 8-CH₃O), evolving from its method of preparation, was confirmed by its dehydrogenation to 3-hydroxy-8-methoxyphenanthrene (VIII) and methylation of the latter to 3,8-dimethoxyphenanthrene (IX), described earlier in the literature [4].

The described results together with the earlier obtained [2] data lead to the conclusion that the presence of the methoxyl group in the meta-position with respect to the point of ring B closure excludes the possibility of a one-step realization of the investigated conversion. In these cases the tricyclic methoxy ketones can be obtained by way of separate closure of rings B and C.



EXPERIMENTAL

β -(*o*-Tolyl)ethylmalonic Ester (III, R = *o*-CH₃). This ester was obtained earlier by Wessely and Wang [5], who gave only the boiling point of the compound. β -(*o*-Tolyl)ethyl bromide (90 g), obtained by the method of Shorygin and Shorygina [6], was condensed with the sodio derivative of malonic ester, prepared from 110 g of this ester and 13 g of sodium in 210 ml of anhydrous alcohol. After two vacuum distillations there was obtained 85 g (67.7%) of colorless oil with b.p. 171-176° at 5 mm (in the literature [5] the indicated b.p. is 185-187° at 9 mm).

d_4^{20} 1.0550, n_D^{20} 1.4930. MR_D 75.82. $C_{16}H_{22}O_4$. Calculated 75.79.

0.1160 g sub.: 0.2920 g CO₂; 0.0856 g H₂O. 0.1054 g sub.: 0.2670 g CO₂; 0.0782 g H₂O. Found %: C 68.65, 69.11; H 8.20, 8.24. $C_{16}H_{22}O_4$. Calculated %: C 69.06; H 7.91.

β -(*o*-Anisyl)ethylmalonic Ester (III, R = *o*-CH₃O). β -(*o*-Anisyl)ethylbromide (143.3 g) was added with stirring to a solution of the sodio derivative of malonic ester, prepared from 160 g of malonic ester and 23 g of sodium in 270 g of anhydrous alcohol. The mixture was boiled for 3 hours, after which the greater part of the alcohol was distilled off, to the cooled solution was added hydrochloric acid-acidified water, the product was dissolved in ether, the solution was washed with water, and then dried over anhydrous sodium sulfate. Vacuum distillation gave 134 g (68.4%) of colorless oil:

B.p. 204-206° (15 mm), d_4^{20} 1.0974, n_D^{20} 1.4966, MR_D 78.33. C₁₆H₂₂O₅. Calculated 77.43.

0.1017 g sub.: 0.2444 g CO₂; 0.0696 g H₂O. Found %: 65.54; H 7.64. C₁₆H₂₂O₅. Calculated %: C 65.31; H 7.48.

β -(*o*-Tolyl)ethyl-(3-chlorocrotyl)malonic Ester (IV, R = *o*-CH₃). To a solution of the sodio ester derivative (III, R = *o*-CH₃), prepared from 83 g of the ester and 7.3 g of sodium in 140 ml of anhydrous alcohol, with water cooling and stirring was added 43 g of freshly distilled 1,3-dichloro-2-butene. The mixture was boiled for 4 hours, after which part of the alcohol was distilled off, to the residue was added hydrochloric acid-acidified water, the product was dissolved in ether, the solution was washed with water, and then dried over sodium sulfate. Vacuum distillation gave 99.3 g (90.75%) of viscous, light yellow liquid:

B.p. 192-196° (2 mm), d_4^{17} 1.0989, n_D^{17} 1.5080, MR_D 99.42. C₂₀H₂₇O₄Cl. Calculated 98.66.

0.1033 g sub.: 0.0416 g AgCl. 0.1047 g sub.: 0.0408 g AgCl. Found %: Cl 9.96, 9.64. C₂₀H₂₇O₄Cl. Calculated %: Cl 9.68.

β -(*o*-Anisyl)ethyl-(3-chlorocrotyl)malonic Ester (IV, R = *o*-CH₃O). In similar manner the condensation of 40 g of the dichlorobutene with the sodio ester derivative (III, R = *o*-CH₃O), prepared from 70 g of the ester and 5.5 g of sodium in 70 ml of anhydrous alcohol, gave 79.2 g (87%) of viscous, almost colorless oil:

B.p. 230-236° (14 mm), d_4^{20} 1.1229, n_D^{20} 1.5090, MR_D 101.70. C₂₀H₂₇O₅Cl. Calculated 100.31.

0.0922 g sub.: 0.0379 g AgCl. 0.1231 g sub.: 0.0470 g AgCl. Found %: Cl 9.49, 9.45. C₂₀H₂₇O₅Cl. Calculated %: Cl 9.28.

β -(*o*-Tolyl)ethyl-(3-chlorocrotyl)malonic Acid (V, R = *o*-CH₃). A mixture of 455 ml of 90% alcohol, 33 g of sodium hydroxide and 95.5 g of the disubstituted malonic ester (IV, R = *o*-CH₃) was boiled under reflux for 4 hours, after which the alcohol was completely removed by distillation, and the cooled alkaline solution was acidified with hydrochloric acid. The separated viscous oil, gradually crystallizing, was dissolved in ether, and the solution was washed with water and dried over sodium sulfate. The crystalline substance remaining after ether removal was washed with benzene, in which it is almost insoluble. The yield of colorless crystals with m.p. 173-174° was 71 g (87.76%).

0.1022 g sub.: 0.0482 g AgCl. 0.1006 g sub.: 0.0466 g AgCl. Found %: Cl 11.67, 11.46. C₁₈H₁₉O₄Cl. Calculated %: Cl 11.43.

β -(*o*-Anisyl)ethyl-(3-chlorocrotyl)malonic Acid (V, R = *o*-CH₃O). In the above described manner the saponification of 79 g of the ester (IV, R = *o*-CH₃O) with a solution of 25 g of sodium hydroxide in 250 ml of moist alcohol gave 63.5 g (94.2%) of benzene-washed colorless crystals with m.p. 161-162°.

0.1023 g sub.: 0.0438 g AgCl. 0.1025 g sub.: 0.0448 g AgCl. Found %: Cl 10.59, 10.81. C₁₈H₁₉O₅Cl. Calculated %: Cl 10.87.

α -(3-Chlorocrotyl)- γ -(*o*-tolyl)butyric Acid (II, R = *o*-CH₃). Twenty grams of the disubstituted malonic acid (V, R = *o*-CH₃) was decarboxylated by heating in a distilling flask until the evolution of carbon dioxide gas had ceased. Distillation of the obtained oil gave 16 g (93.2%) of substance with b.p. 204-205° at 3 mm, completely crystallizing in the receiver. M.p. 51-52°.

0.1033 g sub.: 0.0558 g AgCl. 0.1010 g sub.: 0.0554 g AgCl. Found %: Cl 13.36, 13.57. C₁₈H₁₉O₃Cl. Calculated %: Cl 13.32.

α -(3-Chlorocrotyl)- γ -(*o*-anisyl)butyric Acid (II, R = *o*-CH₃O). The decarboxylation of 30 g of the dibasic acid (V, R = *o*-CH₃O) gave 24.1 g (92.85%) of viscous, light yellow oil:

B.p. 210-215° (10 mm), d_4^{20} 1.1615, n_D^{20} 1.5363, MR_D 75.88. C₁₈H₁₉O₃Cl. Calculated 75.44.

0.1029 g sub.: 0.0497 g AgCl. Found %: Cl 12.43. C₁₈H₁₉O₃Cl. Calculated %: Cl 12.56.

3-Keto-8-methyl-1,2,3,9,10,10a-hexahydrophenanthrene (I, R = 8-CH₃). To 7 g of the acid (II, R = *o*-CH₃) with ice cooling and stirring was gradually added 35 ml of sulfuric acid (d 1.78). The mixture was let stand at room temperature until foaming had ceased, caused by the evolution of hydrogen chloride (about a half hour), after which the

mixture was heated for 5 hours on the water bath (60-75°) in a stream of carbon dioxide gas, and then let stand overnight. When mixed with ice water a crystalline substance separated, which was filtered, rubbed with an excess of 10% sodium hydroxide solution, again filtered, washed with water, and dried. Recrystallization of the crude product (4 g) from alcohol gave 3.5 g (62.95%) of colorless crystals with m.p. 157-158°.

0.1032 g sub.: 0.3207 g CO₂, 0.0745 g H₂O. 0.1053 g sub.: 0.3214 g CO₂, 0.0758 g H₂O. Found %: C 84.75, 84.92; H 8.02, 7.99. C₁₅H₁₆O. Calculated %: C 84.90; H 7.55.

The 2,4-dinitrophenylhydrazone, obtained from 0.3 g of the ketone (I, R = 8-CH₃) and 0.26 g of dinitrophenylhydrazine in alcohol, after recrystallization from chloroform-alcohol mixture, had m.p. 223-224°.

0.0326 g sub.: 4.5 ml N₂ (20°, 678 mm). Found %: N 14.47. C₂₁H₂₀O₄N₄. Calculated %: N 14.29.

3-Hydroxy-8-methylphenanthrene (VI). One gram of the ketone (I, R = 8-CH₃) was dehydrogenated by heating with 0.3 g of sulfur at 180-215° to cessation of hydrogen sulfide evolution (about a half hour). The crystallized dehydrogenated product was dissolved with cooling in 5% alkali, after which the solution was filtered and acidified. Recrystallization of the filtered and dried substance from alcohol (boiled with carbon) gave fluffy, light cream crystals with m.p. 144-145°. Yield 0.5 g (50.9%).

0.0937 g sub.: 0.2961 g CO₂, 0.0520 g H₂O. 0.0907 g sub.: 0.2849 g CO₂, 0.0510 g H₂O. Found %: C 86.18; 86.54; H 6.16, 6.28. C₁₅H₁₂O. Calculated %: C 86.54; H 5.77.

The orange-yellow picrate, obtained from alcohol, had m.p. 180°.

Action of Sulfuric Acid on α -(3-Chlorocrotyl)- γ -(α -anisyl)-butyric Acid. Three grams of the acid (II, R = α -CH₃O) was treated with 18 ml of sulfuric acid (d 1.78) under the conditions described above for the nuclear methylated acid. The mixture was heated in a carbon dioxide stream for 3 hours at 60°. When the red solution was mixed with ice water a dark colored waxy substance separated. This substance failed to dissolve in ether, but dissolved completely on rubbing with a large amount of water, forming a light purple opalescent solution. The substance dissolved immediately in alkali. Any neutral products were completely absent.

2-(3-Chlorocrotyl)-5-methoxy-1-tetralone (VII). To a solution of 10 g of the acid (II, R = α -CH₃O) in 18 ml of dry benzene was added in small portions 7.3 g of phosphorus pentachloride. After vigorous reaction had ceased the greater part of the benzene and the phosphorus oxychloride formed in the reaction were distilled off on the boiling water bath. The rest of the benzene and phosphorus oxychloride was removed *in vacuo* and the gradually raised temperature of the mixture was brought to 180°. At this temperature decomposition set in with the copious evolution of hydrogen chloride. After gas evolution had ceased the residue was dissolved in ether, the solution washed with alkali, then with water, and finally dried over sodium sulfate. Vacuum distillation gave 5.7 g (60.9%) of yellowish viscous oil with b.p. 190° (8 mm).

0.1040 g sub.: 0.0527 g AgCl. 0.1022 g sub.: 0.0565 g AgCl. Found %: Cl 13.97, 13.68. C₁₅H₁₇O₂Cl. Calculated %: Cl 13.42.

This ketone, similar to its 7-methoxy isomer [2], fails to form the semicarbazone, apparently due to the fact that it is an α,α' -substituted cyclohexanone.

3-Keto-8-methoxy-1,2,3,9,10,10a-hexahydrophenanthrene (I, R = 8-CH₃O). The substituted tetralone (VII) (3.4 g) with water cooling was treated with 8 ml of sulfuric acid (d 1.74). The mixture stood at room temperature for 24 hours. When the red solution was mixed with ice water a product separated, which partially crystallized. The substance was dissolved in ether, the solution washed with alkali and water, and dried over sodium sulfate. The crystalline product remaining after ether removal was recrystallized from alcohol. The yield of colorless crystals with m.p. 111-112° was 1.4 g (47.7%).

0.1000 g sub.: 0.2904 g CO₂, 0.0658 g H₂O. 0.1006 g sub.: 0.2911 g CO₂, 0.0664 g H₂O. 0.2220 g sub.: 0.2270 g AgI. Found %: C 79.20, 78.94; H 7.31, 7.33, CH₃O 13.51. C₁₄H₁₃O(OCH₃). Calculated %: C 78.94; H 7.02; CH₃O 13.54.

The 2,4-dinitrophenylhydrozone, obtained from 0.35 g of the methoxy ketone and 0.25 g of phenylhydrazine in alcohol, after recrystallization from a chloroform-alcohol mixture, melted at 233°.

0.1004 g sub.: 13.2 ml N₂ (23.5°, 672 mm). Found %: N 13.39, C₂₁H₂₀O₅N₄. Calculated %: N 13.72.

3-Hydroxy-8-methoxyphenanthrene (VIII). The methoxy ketone (3 g) was dehydrogenated by heating with 1 g of sulfur (180-215° 1 hour). The crystalline dehydrogenation product was dissolved in alkali, the solution filtered, acidified, the precipitated substance washed with water, and dried. Recrystallization of the product from methyl alcohol

(boiling with carbon) and from water gave 1.7 g (57.8%) of colorless crystals with m.p. 170-171°.

0.0621 g. sub.: 0.1822 g CO₂; 0.0298 g H₂O. 0.0640 g sub.: 0.1882 g CO₂; 0.0318 g H₂O. Found %: C 80.00, 80.19; H 5.33, 5.52. C₁₈H₁₂O₂. Calculated %: C 80.35; H 5.35.

3,8-Dimethoxyphenanthrene (IX). To a solution of 0.5 g of 3-hydroxy-8-methoxyphenanthrene in 18 ml of 2% sodium hydroxide, heated on the water bath, was added dropwise 0.8 g of dimethyl sulfate. The mixture was heated for 15 minutes, after which 15 ml of 4% sodium hydroxide solution was added and the heating continued another 15 minutes. After cooling, the crystalline product was filtered and washed with water. The yield of methyl alcohol re-crystallized colorless crystals with m.p. 116-117° was 0.4 g (75.4%) (the literature [4] for 3,8-dimethoxyphenanthrene gives m.p. 117°).

SUMMARY

1. The influence of the methyl and methoxyl groups, found in the ortho-position of the aromatic nucleus, on the sulfuric acid hydrolysis and double cyclization of α -(3-chlorocrotyl)- γ -phenylbutyric acids was investigated.
2. It was shown that the methyl group fails to exert substantial influence on the course of the investigated transformation; the cyclization product - 3 keto-8-methylhexahydrophenanthrene - is obtained in a yield of the same order as that of the unsubstituted ketone and its other methyl homologs.
3. The presence of a methoxyl group in the ortho-position excludes the possibility of realizing the investigated transformation in one stage; in this case, as in the case where the same group is present in the para-position, the tricyclic methoxy ketone can be obtained by way of separate closure of rings B and C.

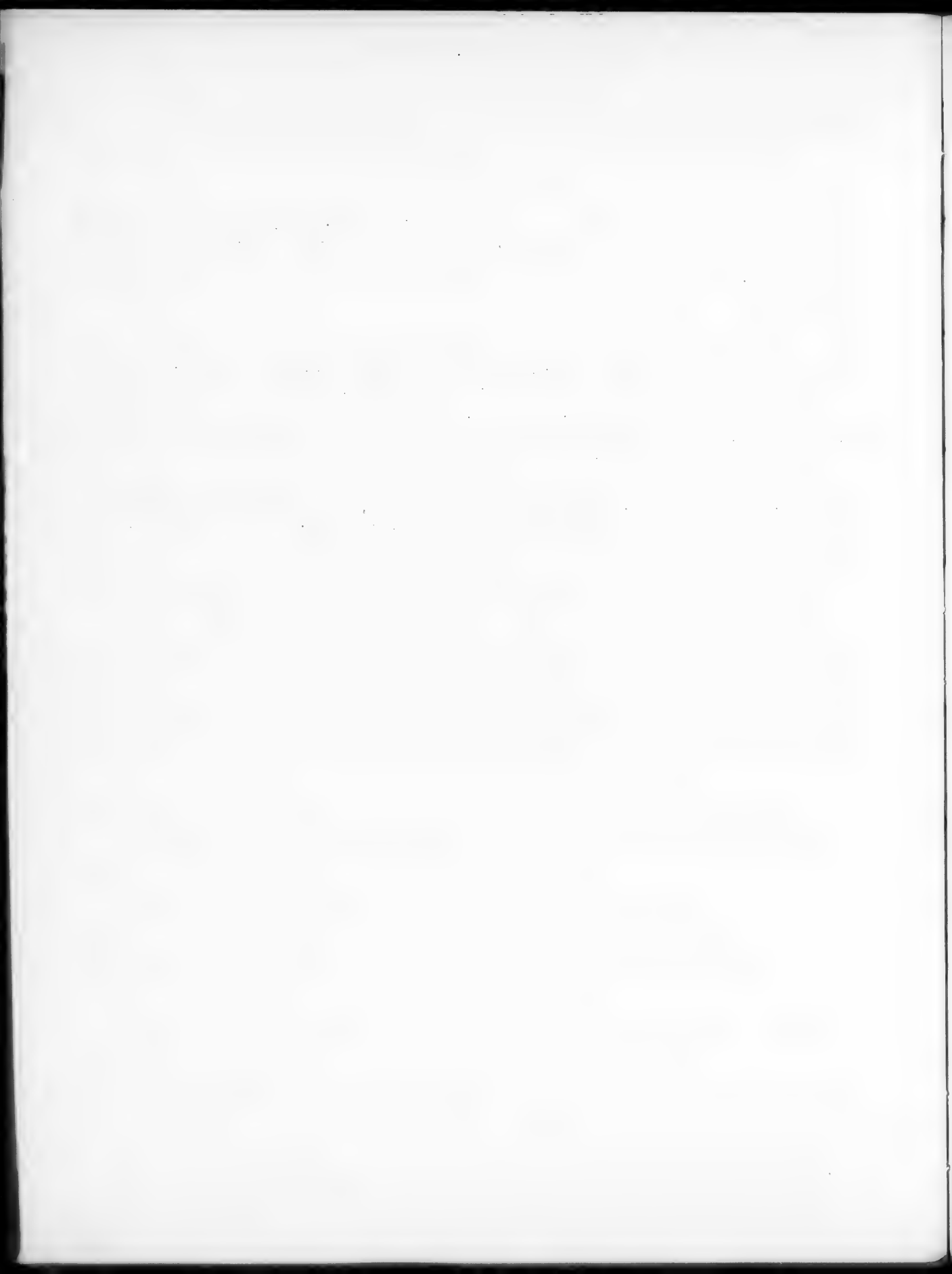
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PREPARATION OF SOME 3-ARYLOXAZOLIDINES

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The condensation of N-(β -hydroxyethyl)arylamines with aldehydes, leading to 3-aryloxazolidines, up to now has been studied only for the examples N-(β -hydroxyethyl)aniline and N-(β -hydroxyethyl)-*p*-phenetidine.

Thus, Bergmann, Ulpts and Camacho [1], on heating these aryloethanolamines with formalin and with benzaldehyde obtained 3-phenyloxazolidine, 3-*p*-phenetyloxazolidine and 2-phenyl-3-*p*-phenetyloxazolidine. 3-Phenyloxazolidine was also described by Kon and Roberts [2]. In 1952 Zimkin and Bergmann [3] described the preparation of 3-phenyloxazolidine, and also 2-methyl-, 2-ethyl-, 2-propyl-, 2-(2'-ethyl)hexyl- and 2,3-diphenyloxazolidine.

The formation of the oxazolidine cycle proceeds under mild conditions and depends but slightly on the structure of the aldehyde. Thus, the condensation of N-(β -hydroxyethyl)aniline with acetaldehyde proceeds at room temperature in ether solution; with other aldehydes the formation of the oxazolidines proceeds under the removal of the reaction water by distillation with benzene.

In their work on the synthesis of N-substituted 2-aryl-oxazolidines, Ushenko, Baranov and Gorizdra [4] introduced into the reaction with N-(β -hydroxyethyl)aniline the aldehydes benzaldehyde, *o*-chlorobenzaldehyde and also *m*-nitrobenzaldehyde, and obtained the corresponding 2,3-diphenyloxazolidine, 2-*o*-chlorophenyl-3-phenyloxazolidine and 2-*m*-nitrophenyl-3-phenyloxazolidine. Petrov and Gosteva [5] obtained 2-furyl-3-phenyloxazolidine by pouring together over 10 minutes molar amounts of furfural and N-(β -hydroxyethyl)aniline in the presence of 1 g of potash. The attempts of Kiprianov and Rozhkova [6] to condense N-(β -hydroxyethyl)aniline with ketones gave negative results.

In the present work it was shown by us that N-(β -hydroxyethyl)-*o*-toluidine, N-(β -hydroxyethyl)-*p*-toluidine and N-(β -hydroxyethyl)-*p*-anisidine condense with benzaldehyde in the same manner as N-(β -hydroxyethyl)aniline [3,4]. When the water was removed from the reaction mixture by distillation with benzene there were obtained in good yields 2-phenyl-3-*p*-tolyloxazolidine and 2-phenyl-3-*p*-anisylloxazolidine, and in lower yield 2-phenyl-3-*o*-tolyloxazolidine.

From the mixture of N-(β -hydroxyethyl)-*p*-toluidine with acetaldehyde in ether after one day standing at room temperature there was obtained 2-methyl-3-*p*-tolyloxazolidine. It should be mentioned that N-(β -hydroxyethyl)-*o*-toluidine fails to react with acetaldehyde under these conditions, while in the reaction with benzaldehyde the 2-phenyl-3-*o*-tolyloxazolidine is obtained in half the yield of the 2-phenyl-3-*p*-tolyloxazolidine.

The heating of N-(β -hydroxyethyl)-*p*-toluidine with 30% formalin led to the formation of 3-*p*-tolyloxazolidine.



EXPERIMENTAL

3-*p*-Tolyloxazolidine. A mixture of 15 g of N-(β -hydroxyethyl)-*p*-toluidine and 10 ml of 30% formalin was heated for 1 hour on the water bath under reflux. Cooling of the reaction mixture gave crystals, which were filtered and washed with ether. Recrystallization from petroleum ether gave 14.7 g of 3-*p*-tolyloxazolidine (89.5%) with m.p. 61.5°. Not described in the literature.

Found %: N 8.67, 8.59. C₁₀H₁₃ON. Calculated %: N 8.59.

2-Methyl-3-*p*-tolyloxazolidine. Fifteen grams of N-(β -hydroxyethyl)-*p*-toluidine was mixed with 4.6 g of acetaldehyde in 50 ml of anhydrous ether and let stand 24 hours. After removing the water the ether solution was dried over calcined potash. After distilling off the ether the residue was vacuum distilled to give: 1.2 g of fraction with m.p. 42°, being unchanged N-(β -hydroxyethyl)-*p*-toluidine, and 12.3 g (80% of the theoretical, based on reacted ethanol-*p*-toluidine) of an oil with slight odor, being 2-methyl-3-*p*-tolyloxazolidine. Not described in the literature.

B.p. 121.5-122° (9 mm), n_D^{20} 1.5540, d_4^{20} 1.0484, M_R 54.18. C₁₁H₁₅ON. Calculated 53.86.

Found %: N 8.21, 8.41. C₁₁H₁₅ON. Calculated %: N 7.90.

2-Phenyl-3-p-tolyloxazolidine. A mixture of 30 g of N-(β -hydroxyethyl)-p-toluidine and 21.5 g of benzaldehyde in 100 ml of benzene was boiled for 6 hours until the water present in the mixture was completely removed. Amount of removed water 3 g. After distilling off the benzene the residue crystallized to give 43.2 g (91%) of crude 2-phenyl-3-p-tolyloxazolidine, melting at 61°. After recrystallization from petroleum ether the substance melted at 71° and was pure 2-phenyl-3-p-tolyloxazolidine. Not known in the literature.

Found %: N 5.81, 5.86. $C_{16}H_{17}ON$. Calculated %: N 5.85.

2-Phenyl-3-o-tolyloxazolidine. A mixture of 15 g of N-(β -hydroxyethyl)-o-toluidine and 10.8 g of benzaldehyde in 100 ml of benzene was boiled for 8 hours until all of the water was removed. About 1g of water was collected. After distilling off the benzene the residue (23 g of oil) was vacuum distilled through a fractionation column to give the 2-phenyl-3-o-tolyloxazolidine. Yield 6.5 g (38%). Not described in the literature

B.p. 147-148° (2 mm), n_D^{20} 1.5853, d_4^{20} 1.1032, MR_D 72.76. $C_{16}H_{17}ON$. Calculated 72.27.

Found %: N 6.18, 6.29. $C_{16}H_{17}ON$. Calculated %: N 5.86.

2-Phenyl-3-p-anisylloxazolidine. A mixture of 8.3 g of N-(β -hydroxyethyl)-p-anisidine and 5.3 g of benzaldehyde in 100 ml of benzene was boiled for 6 hours to distill off the water. Amount of collected water 0.9 g. The residue crystallized after removal of the benzene by distillation. After recrystallization from petroleum ether the substance melted at 60-60.5° and was 2-phenyl-3-p-anisylloxazolidine. Yield 10.2 g (80%). Not described in the literature.

Found %: N 5.67, 5.68. $C_{16}H_{17}O_2N$. Calculated %: N 5.45.

SUMMARY

1. The unknown 2-methyl-3-p-tolyloxazolidine, 2-phenyl-3-p-tolyloxazolidine, 2-phenyl-3-o-tolyloxazolidine and 2-phenyl-3-p-anisylloxazolidine were prepared.

2. N-(β -Hydroxyethyl)-o-toluidine, in contrast to N-(β -hydroxyethyl)-p-toluidine, fails to react with acetaldehyde at room temperature in ether and in the reaction with benzaldehyde gives 2-phenyl-3-o-tolyloxazolidine in one half the yield of 2-phenyl-3-p-tolyloxazolidine.

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β - LACTONES AND β - LACTONO ACIDS

XI. REFORMATSKY REACTION WITH BROMOMALONIC ESTER

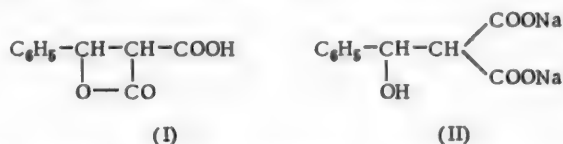
II. BENZALMALONO-β -LACTONE

N. S. Wulfson

In one of the previous communications [1], on the example of condensing acetone with mixed malonic acetic anhydride, it was shown by us that the intermediate product in the formation of the β -lactone of isopropylidenemalonamic acid is the mixed anhydride of β -hydroxyisopropylmalonic and acetic acids. This compound proved to be extremely unstable and could not be isolated in the pure form. We judged its formation by means of indirect reactions.

In another of our papers [2] it was shown that in the Reformatsky reaction between benzaldehyde and bromomalonic ester the ester of β -hydroxybenzmalonic acid is formed in the first step, which is easily dehydrated, and the ester of benzmalonic acid is isolated as the final reaction product. However, under mild saponification of the reaction product with an alcoholic sodium hydroxide solution we obtained the sodium salt, the analysis of which well agreed with that calculated for the salt of β -hydroxybenzylmalonic acid.

On the basis of earlier expressed representations as to the mechanism for the formation of β -lactono acids [1], we postulated that in the reaction of the sodium salt of the β -hydroxydicarboxylic acid with acetyl chloride the mixed anhydride of β -hydroxybenzylmalonic and acetic acids should be obtained, which under the proper conditions should lead to the formation of the β -lactone of benzmalonic acid (I).



Actually, on adding 2 moles of acetyl chloride to a suspension of the sodium salt (obtained by mild saponification of the condensation product from bromomalonic ester and benzaldehyde in the presence of zinc) in anhydrous ether the β -lactone of benzmalonic acid (I) was isolated, identical with the product described in the literature [3] and obtained by us in earlier studies [1,4].

It was shown by us earlier [1] that in the action of acetyl chloride on the silver salt of benzmalonic acid the β -lactono acid (I) is not formed. As a result, the preparation of the β -lactone of benzmalonic acid described in this paper confirms the validity of our conclusion on the formation of the ester of β -hydroxybenzylmalonic acid from benzaldehyde and bromomalonic ester by the Reformatsky reaction. In addition, the described experiments again support the validity of the scheme, proposed by us for the reaction mechanism involved in the formation of β -lactono acids.

EXPERIMENTAL

Preparation of the Sodium Salt of β -Hydroxybenzylmalonic Acid. (II). In a 100 ml round-bottomed flask with stirrer and reflux condenser was boiled a mixture of 10.6 g of freshly distilled (*in vacuo*) benzaldehyde, 24 g of bromomalonic ester, 50 ml of dry benzene and 6.55 g of zinc turnings (etched with 10 % hydrochloric acid, washed with water, methanol and acetone, dried, and heated with an iodine crystal). The clear colorless solution gradually became cloudy and turned brown. Reaction was not too vigorous, but considerable zinc dissolved. The mixture was heated with stirring for 3 hours. Toward the end of heating a fairly copious, white, amorphous precipitate was obtained. After cooling the reaction mass was decomposed with 100 ml of 10% sulfuric acid. There remained 0.6 g of unreacted zinc. The benzene solution was washed twice with 50 ml portions of sodium bisulfite solution, 10% soda solution, repeatedly with water to neutrality of the wash liquors, and dried over magnesium sulfate. To the benzene solution was added 100 ml of 5% alcoholic sodium hydroxide solution and the whole let stand overnight at room temperature. The precipitate was filtered, washed with alcohol and recrystallized from 70% alcohol. Yield of sodium salt (II) 16 g.

0.0770, 0.0476, 0.1615 g sub.: 0.0432, 0.026, 0.0895 g Na₂SO₄. Found %: Na 18.18, 17.85, 17.94. C₁₀H₈O₆Na₂. Calculated %: Na 18.07.

Preparation of Benzalmalono- β -Lactone (I). To a suspension of 5.08 g of the sodium salt (II) in 50 ml of dry ether was added dropwise at temperature not over 25° and with stirring 3.14 g of acetyl chloride. Stirring was maintained for 15 minutes, the sodium chloride precipitate was filtered, washed with dry ether, and the combined ether solutions let stand overnight. The ether was removed in vacuo, while the residue was recrystallized from acetone-benzene mixture. Yield 2.7 g (70.3%, based on sodium salt (II), or 47%, based on benzaldehyde). M.p. 145-146°. The mixed melting point with the β -lactone of benzalmalonic acid, obtained by other methods [1,4], failed to be depressed.

0.0752 g sub.: (dissolved in 15 ml of 70% alcohol): 3.87 ml 0.1 N NaOH. $C_{10}H_8O_4$. Calculated for monobasic acid: 3.92 ml NaOH.

SUMMARY

The reaction of acetyl chloride with the sodium salt, formed in the saponification of the condensation product from benzaldehyde and bromomalonic ester (Reformatsky reaction), gave the β -lactone of benzalmalonic acid. In that way it was shown that the Reformatsky reaction between benzaldehyde and bromomalonic ester gives the ester of β -hydroxybenzylmalonic acid. In addition, it was again experimentally confirmed that the intermediate product in the reaction for the formation of β -lactono acids is the mixed anhydride of β -hydroxyalkyl (ovaryl) malonic and acetic acids.

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POLYMERIZATION OF SOME UNSATURATED ESTERS OF
PHOSPHONOCARBOXYLIC ACIDS

Gilm Kamai and V. A. Kukhtin

In an earlier published paper [1] it was shown by us that the allyl esters of acetylphosphinic and benzoylphosphinic acids can be polymerized when heated, forming gel polymers. These same esters also readily copolymerize with methyl methacrylate, forming fire-resistant copolymers.

The synthesis of some new unsaturated esters of phosphonocarboxylic acids and the results of studying their polymerization tendency are described in the present paper.

TABLE 1

Exp. No.	Ester	Organo-phosphorus addition (in %)	Time of polymerization (in hours)	Brinell Hardness (kg/sq. mm)	Heat resistance (in °C)	Specific impact viscosity (kg · cm/sq. cm)	Clarity (in %)
1	$(C_2H_5O)_2P(=O)CH_2COOC_3H_5$	5	7.5	11.2	88	—	—
2	$(C_2H_5O)_2P(=O)CH_2COOC_3H_5$	10	9	10.4	74	12	91.5
3	$(C_2H_5O)_2P(=O)CH_2COOC_3H_5$	15	12	11.9	62	—	91.5
4	$(C_2H_5O)_2P(=O)CH_2COOC_3H_5$	20	16	7.4	49	16	89.5
5	$(CH_3O)_2P(=O)CH_2COOC_3H_5$	15	16	11.2	65	12.5	91.7
6	$iso-(C_3H_7O)_2P(=O)CH_2COOC_3H_5$	15	18	12.3	72	11.4	91.5
7	$N-(C_4H_9O)_2P(=O)CH_2COOC_3H_5$	15	17	12.9	63	13.3	92.4
8	$iso-(C_4H_9O)_2P(=O)CH_2COOC_3H_5$	15	20	14	67	13	91.5

We synthesized the unsaturated esters of phosphonocarboxylic acids by the usual methods [2,3]. Some of the physical constants of the obtained compounds are given in Table 3.

The esters of phosphonoacetic acid with one allyl group at the carbon (Table 3, Compounds 1-5) showed slight inclination to polymerize. Only the first three esters under prolonged heating with benzoyl peroxide form low-molecular polymers (with $\bar{n} = 2-4$ for the degree of polymerization). The polymerization of these esters was run at 60-70° for a period of 200 hours with the addition of 1% (by weight) of benzoyl peroxide.

We prepared a number of copolymers of these esters with methyl methacrylate and studied their properties. All of the obtained copolymers are hard, transparent, colorless or slightly yellow resins. The copolymers have a low-hardness and poor heat resistance. Copolymers, containing 15 and 20% of the organophosphorus component, are quickly self-extinguishing after removal of the flame.

The physical and mechanical properties of the copolymers are given in Table 1.

TABLE 2

Exp. No.	Ester	Organo-phosphorus addition (in %)	Time of polymerization (in hours)	Brinell Hardness (kg/ sq. mm)	Heat resistance (in °C)	Specific impact viscosity (kg · cm/ sq. cm)	Clarity (in %)
1	$(C_3H_5O)_2P(=O)CH_2COOC_2H_5$	10	20	9	65	91.2	10.3
2	$(C_3H_5O)_2P(=O)CH_2COOC_2H_5$	20	28	8.9	74	92	7.8
3	$(C_3H_5O)_2P(=O)CH_2COOC_2H_5$	30	37	4.7	48	91.7	12
4	$(C_3H_5O)_2P(=O)CH_2COOC_2H_5$	40	46	—	—	—	—
5	$(C_3H_5O)_2P(=O)CH_2COOC_2H_5$	50	53	—	—	—	—
6	$(C_3H_5O)_2P(=O)CH_2COOCH_3$	25	26	8	56	92	—
7	$(C_3H_5O)_2P(=O)CH_2COOC_4H_9-iso$	25	20	10.3	65	91.5	6.4
8	$(C_3H_5O)_2P(=O)COOC_2H_5$	20	11	12.1	60	92	—
9	$(C_3H_5O)_2P(=O)COOC_2H_5$	30	17	4.5	36	90.5	10.9

TABLE 3

Exp. No.	Ester	Boiling point at pressure (in mm)	n_D^{20}	d_4^{20}	P content in %	
					Calculated	Found
1	$(CH_3O)_2P(=O)CH_2COOC_3H_7$	114 - 114.5 (2)	1.4505	1.2064	14.83	14.53
2	$(C_2H_5O)_2P(=O)CH_2COOC_3H_7$	157 - 158 (10)	1.4426	1.1203	13.54	13.87
3	$iso-(C_3H_7O)_2P(=O)CH_2COOC_3H_7$	152 - 153 (6)	1.4357	at 15° 1.0520	11.71	11.60
4	$N-(C_4H_9O)_2P(=O)CH_2COOC_3H_7$	146 - 147.5 (1)	1.4470	at 15° 1.0492	10.59	10.42
5	$iso-(C_4H_9O)_2P(=O)CH_2COOC_3H_7$	154 - 156 (4)	1.4438	at 15° 1.0356	10.59	10.21
6	$(C_3H_5O)_2P(=O)CH_2COOCH_3$	128 - 129 (3)	1.4578	1.1478	13.22	13.17
7	$(C_3H_5O)_2P(=O)CH_2COOC_2H_5$	133 - 134 (3)	1.4521	1.1186	—	—
8	$(C_3H_5O)_2P(=O)CH_2COOC_3H_7-iso$	150 - 151 (5)	1.4545	1.0983	11.81	11.94
9	$(C_3H_5O)_2P(=O)CH_2COOC_4H_9-iso$	130 - 131 (1)	1.4560	1.0850	11.21	11.29
10	$(C_3H_5O)_2P(=O)CH_2COOC_4H_9-N$	142 - 143 (1.5)	1.4552	1.0801	11.21	11.39
11	$(C_3H_5O)_2P(=O)CH_2COOC_3H_7$	165 - 166 (9)	1.4711	1.0967	11.82	11.69
12	$(C_3H_5O)_2P(=O)CH_2COOC_2H_5$	107 - 108 (2)	1.4576	1.0512	12.58	12.61
13	$(C_2H_5O)_2P(=O)CH_2COOC_2H_5$	103 - 104 (2.5)	1.4340	1.1190	13.93	14.04
14	$(C_3H_5O)_2P(=O)COOC_2H_5$	126 - 127 (3)	1.4490	1.1204	—	—

The phosphonocarboxylic esters with two allyl groups at the phosphorus (Table 3, Compounds 6-10 and 14) under heating in the presence of 1% benzoyl peroxide form transparent gel polymers, insoluble in organic solvents. The duration of polymerization for these esters at 70° was 70-100 hours for the phosphonoacetates and 40-50 hours for the phosphonoformate.

We prepared a number of copolymers of these esters with methyl methacrylate and studied their properties. The copolymers, containing 10 and 20% by weight of the phosphonoacetate, possess reduced inflammability.

With increase in the phosphorus content the hardness and heat resistance of the copolymers are reduced. In contrast to the esters with one allyl group, the esters with two allyl groups markedly lower the specific impact viscosity.

The obtained copolymers are poorly soluble in organic solvents. Thus, for example, Copolymer 1 (Table 2) in 24 hours at room temperature dissolves in acetone to the extent of only 12.1%, and Copolymer 2 under the same conditions to the extent of 13.8%.

The physical and mechanical properties of the copolymers are given in Table 2.

The allyl ester of diallylphosphonoacetic acid (Table 3, Compound 11), containing 3 double bonds in its molecule, strongly differs from the other esters in its polymerization properties. When heated with benzoyl peroxide in the air it quickly turns dark red and fails to polymerize. The color changes much more slowly in a nitrogen atmosphere; however, here also polymerization fails to occur and the product retains its original consistency. Similar properties are also possessed by the vinyl ester of diallylphosphonoacetic acid (Table 3, Compound 12). The vinyl ester of diethylphosphonoacetic acid (Table 3, Compound 13) polymerizes in the same way as the allyl ester of the same acid, forming a low-molecular sticky polymer.

EXPERIMENTAL

Synthesis of the Allyl Ester of Dimethylphosphonoacetic Acid.

In a round-bottomed flask fitted with reflux condenser was placed 62 g of trimethyl phosphite and 67 g of allyl chloroacetate. The reaction flask was heated at 110-120° for 4 hours. In this time 21.5 g of methyl chloride was evolved (86%). After three distillations 22.5 g of substance was collected.

B.p. 114-114.5° (2 mm), d_4^{20} 1.2064, n_D^{20} 1.4505, MR_D 46.48; calculated 46.58.

Found %: P 14.53, 14.32. $C_7H_{13}O_3P$. Calculated %: P 14.83.

All of the other esters were obtained in similar manner, with the exception of the diethyl- and diisopropylphosphonoacetates.

Synthesis of the Allyl Ester of Diethylphosphonoacetic Acid.

In a 500 ml three-necked flask, fitted with reflux condenser, stirrer and dropping funnel, was placed 200 ml of dry ether, and 5.3 g of metallic sodium (as wire) was introduced. Then with cooling 31 g of diethylphosphorous acid was added, after which the reaction mass was heated on the water bath for 30 minutes. After cooling to room temperature, to the flask with reaction mixture was added with constant stirring 30 g of allyl chloroacetate. The obtained sodium chloride precipitate was coagulated by boiling with activated carbon for 1 hour. After removal of the sodium chloride and distilling off the solvent a 2-fold vacuum distillation of the residue gave 29 g (55%) of reaction product.

B.p. 157-158° (10 mm), d_4^{20} 1.1203, d_4^{20} 1.1387, n_D^{20} 1.4426, MR_D 56.28; calculated 55.82.

Found %: P 13.87, 13.93. $C_8H_{17}O_3P$. Calculated %: P 13.54.

The allyl ester of diisopropylphosphonoacetic acid was obtained in similar manner.

The physical constants of all of the obtained compounds are given in Table 3.

Polymerization of Unsaturated Esters of Phosphonocarboxylic Acids.

The polymerization experiments were run as follows. Four grams of the investigated ester was placed in a test tube and 0.04 g (1% by weight) of benzoyl peroxide was added. Then the test tube was filled with nitrogen and tightly stoppered with a rubber stopper. The polymerization was run in a thermostat at 70°.

The mixture of monomers was first placed in a flask with ground-glass stopper. To the investigated mixture was added 0.3% by weight of benzoyl peroxide, after which the flask was filled with nitrogen and placed in the thermostat.

Heating at 50-55° was maintained until the mixture of monomers was converted into a thick sirup, after which the obtained sirup was poured into the mold and heated at 50° to complete loss of fluidity.

Elevation of the temperature at this stage to above 50° can lead to the appearance of bubbles. As the copolymer hardened the temperature was gradually raised to 60-70° and it was maintained at this level until polymerization was complete.

SUMMARY

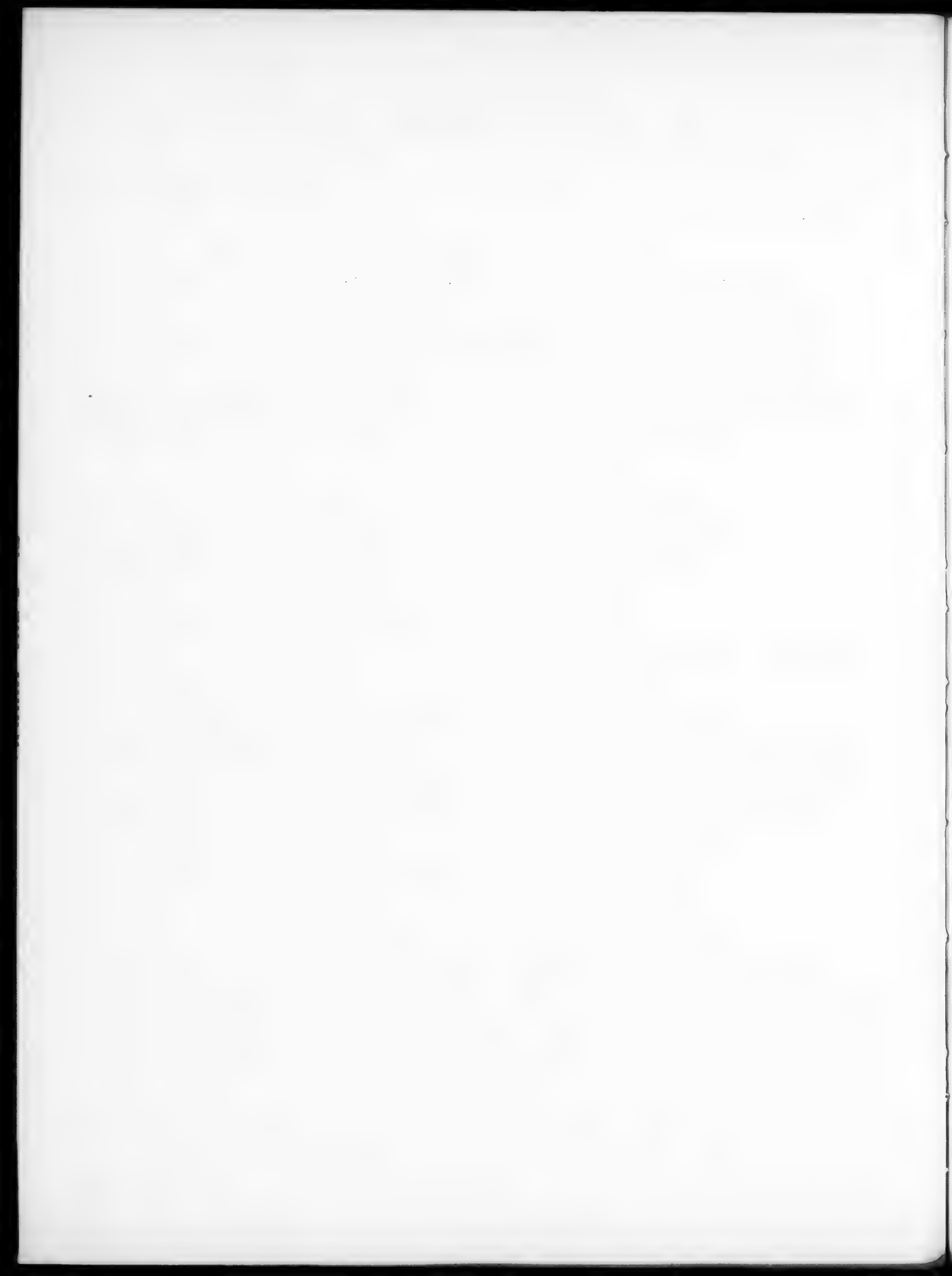
1. A number of new unsaturated esters of phosphonocarboxylic acids were synthesized and a study made of their polymerization tendency.
2. Copolymers of the unsaturated esters of phosphonocarboxylic acids with methyl methacrylate were prepared and their properties described.

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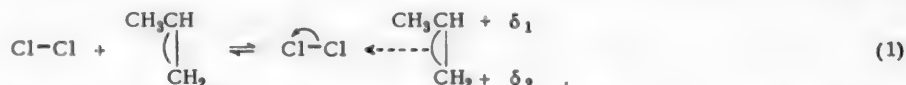


CONJUGATION REACTIONS OF HALOGEN ADDITION TO OLEFINS

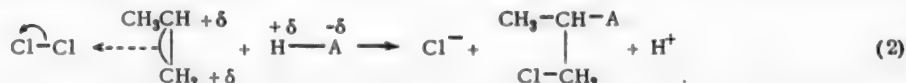
III. ORDER OF ADDITION TO UNSYMMETRICAL OLEFINS

A. I. Titov and F. L. Maklyaev

The order of addition to olefins, for example to propylene, in conjugation reactions can be determined by considering the influence of substituents on the positive charge distribution in the intermediate complex of halogen with olefin [1,2].



Since the methyl group stabilizes the positive charge on the adjacent carbon, then $\delta_1 > \delta_2$ and the addition of anion A^- should proceed in the following order:

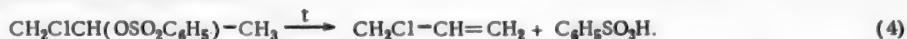


Actually, our studies on the reaction of chlorine with propylene in either formic or acetic acid medium revealed that the reaction products are compounds of type $\text{CH}_2\text{ClCH}_2\text{A}$, being respectively β -chloroisopropyl formate $\text{CH}_2\text{Cl}-\text{CH}(\text{CH}_3)-\text{OCHO}$ and β -chloroisopropyl acetate $\text{CH}_2\text{Cl}-\text{CH}(\text{CH}_3)\text{OCOCH}_3$. To be sure, due to reaction of the complex with chlorine, 1,2-dichloropropane was also formed.

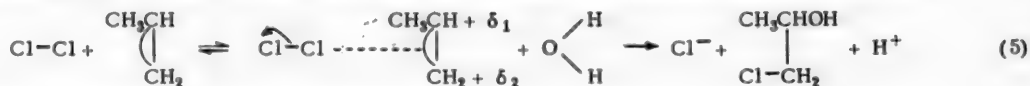
As a result, it was established that a mixture of halogen and propylene under suitable conditions can serve as a β -haloisopropylating agent. In accord with this the reaction of chlorine with propylene in molten benzenesulfonic acid leads to the formation of β -chloroisopropyl benzenesulfonate



This conclusion was confirmed by the ease with which the reaction product decomposed when heated in the presence of acids with the formation of allyl chloride



The reaction between halogen and propylene in water proceeds, according to our views, also through the intermediate creation of a complex of Type (1). Here the predominant formation of β -haloisopropyl alcohols



speaks in favor of our interpretation of the reaction mechanism.

The order of addition in conjugation reactions to other unsymmetrical olefins can be determined in the same manner. Thus, taking into account the favorable influence of the phenyl group in stabilizing the positive charge on the carbon connected to it, it follows that the products of addition to styrene, in accord with the experimental data, will have the structure of type $\text{C}_6\text{H}_5\text{CH}_2\text{A}-\text{CH}_2\text{Cl}$.

As regards the order of addition, in conjugation reactions the halogen atom corresponds to the hydrogen atom in those cases where the addition of hydrogen halide acids is of the ionic type. This analogy can be used for practical purposes. The well-known Markovnikov rule can be used with success here.

EXPERIMENTAL

1. Preparation of β -Chloroisopropyl Acetate. Into a 150 ml reactor was poured 100 g of glacial acetic acid and with vigorous agitation there was simultaneously passed for 2 hours about 15 liters of chlorine and a slightly larger

amount of propylene. The reaction mass was mixed with water and strong sodium hydroxide solution was added to slight alkalinity. After washing with water and drying over calcium chloride the organic layer was fractionally distilled through a dephlegmator. The following fractions were collected: 1st) 95-110°, 17.1 g; 2nd) 110-145°, 5.0 g; 3rd) 145-150°, 21.7 g. Redistillation gave a fraction with b.p. 149-150°, being β -chloroisopropyl acetate [3].

d_4^{20} 1.1012, n_D^{20} 1.4270, MR_D 31.87; calculated 31.83.
Found %: Cl 25.97. $C_5H_9O_2Cl$. Calculated %: C 25.89.

On heating the ester with sodium iodide in acetone solution, and then the iodo derivative with silver nitrate, a product was obtained that gave the characteristic reactions of a primary nitro compound and we failed to reveal the presence of any other possible isomer.

2. Preparation of β -Chloroisopropyl Formate and β -Chloroisopropyl Alcohol. The conjugation reaction of propylene with chlorine in a solution of 92 g of formic acid (d 1.22) was run the same as the just described experiment. Fractional distillation gave the following fractions: 1st) 95-125°, 12.2 g; 2nd) 125-136°, 3.4 g; 3rd) 136-138°, 19.4 g.

The 3rd fraction was the earlier unknown β -chloroisopropyl formate.

B.p. 137°, d_4^{20} 1.1489, n_D^{20} 1.4260, MR_D 27.32; calculated 27.19.
Found %: Cl 28.77. $C_4H_7O_2Cl$. Calculated %: Cl 28.94.

The obtained ester, similar to the acetate, can be converted into the primary nitro compound. When heated with excess 3% hydrogen chloride solution in methyl alcohol it is almost quantitatively converted into methyl formate and β -chloroisopropyl alcohol [4,5].

B.p. 126° (743 mm), d_4^{20} 1.111, n_D^{20} 1.4390.

3. Preparation of β -Chloroisopropyl Benzenesulfonate. The reaction was run in the same apparatus. Through the melt of 144 g of anhydrous benzenesulfonic acid at 65° there was passed for 2.5 hours about 20 liters of chlorine and a slightly larger amount of propylene. After suitable treatment [2] there was obtained 24.2 g of dichloropropane and 128 g (over 50%) of crude ester. When the distillation of large amounts was attempted the ester readily decomposed with the formation of benzenesulfonic acid in the residue and a mixture of 1-chloropropene with allyl chloride in the distillate; rapid distillation of 20-30 g batches at 3-4 mm was entirely satisfactory and proceeded with hardly any residue at 160-170°.

d_4^{20} 1.3014, n_D^{20} 1.5220, MR_D 54.97; calculated 54.84.
Found %: Cl 14.70. $C_9H_{11}O_3SCl$. Calculated %: Cl 15.12.

SUMMARY

In accord with the theories for conjugation addition reactions it was shown that β -chloroisopropyl formate, the acetate and the benzenesulfonate are formed when chlorine reacts with propylene in the respective acids.

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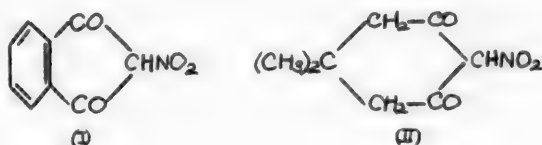
* Consultants Bureau Translation, p. 1607

** Consultants Bureau Translation, p. 1613

NITRODIMEDON AND SOME OF ITS DERIVATIVES

E. Gudrinietse, O. Neiland and G. Vanag

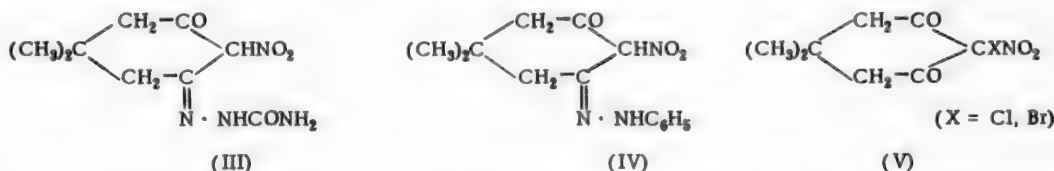
2-Nitro-1,3-indandione (I) is not only an excellent analytical reagent [1,2], but is also the starting material for the synthesis of a number of new compounds [2-5]; consequently it was of interest in this respect to also study other cyclic β -diketones, nitrated at the active methylene group. A comparatively readily available cyclic β -diketone is dimedon, or 1,1-dimethyl-3,5-cyclohexanedione. Its nitro derivative (II) is already known in the literature and is obtained by the nitration of dimedon with nitrogen oxides. We were able to obtain nitrodimedon in slightly better than 50 % yield by the nitration of dimedon with fuming nitric acid. The compound was obtained as colorless crystals with m.p. 105°; water solutions are colored yellow.



Nitrodimedon, the same as nitroindandione, is a strong acid. It readily forms salts, usually quite soluble in water. Some of the organic salts of nitrodimedon have already been described in the literature [6]. We prepared a number of unknown inorganic salts of nitrodimedon, and also a number of salts with organic bases. The bivalent iron salt, being so characteristic for nitroindandione [7], is also characteristic for nitrodimedon. In contrast to all of the other nitrodimedon salts it is dark purple in color; in water it dissolves with a green color.

The salts of nitrodimedon with organic bases, even with the primary aromatic amines, are soluble in water; this means that nitrodimedon is less suitable than nitroindandione for separating these amines from solutions. The salts of some of the tertiary amines separate as oils, which was also observed for some of the tertiary amine salts of nitroindandione [8].

As a ketone nitrodimedon forms the monosemicarbazone (III) and the monophenylhydrazone (IV), both readily soluble in water.



Similar to nitroindandione, nitrodimedon is readily brominated and chlorinated. The obtained halogenated derivatives (V) in aqueous solutions are decomposed with the cleavage of hypochlorous or hypobromous acid.

It is known that dimedon is a reagent for aldehydes; nitrodimedon with aldehydes fails to give any characteristic reactions.

EXPERIMENTAL

4-Nitro-1,1-dimethyl-3,5-cyclohexanedione (Nitrodimedon) (II)

In a three-necked round-bottomed flask with stirrer (with mercury seal), dropping funnel and reflux condenser was placed 20 g of well crushed dimedon and 80 ml of diethyl ether. The flask was immersed in a cooling mixture (ice and salt) and with vigorous stirring from the dropping funnel was added 12 ml of fuming nitric acid ($d \approx 1.5$). After this the reaction mass was stirred without cooling until the brown color had disappeared. Then another 3-5 ml of the

same nitric acid was added. Violent reaction takes place and the flask has to be cooled (with ice and salt). Usually the flask contents become colorless. The ether is removed in vacuo (water-jet pump) at room temperature. The flask contents crystallize into a hard mass. The crystals are separated and washed with a little ether. Yield of nitrodimedon 14 g (56.3 %). M.p. 102°.

3.229 mg sub.: 0.202 ml N_2 (16°, 772 mm). Found %: N 7.51. $C_8H_{11}O_4N$. Calculated %: N 7.57.

Nitrodimedon can be recrystallized from ether-gasoline mixture. Colorless prisms with m.p. 105°. Nitrodimedon is readily soluble in water, alcohol, benzene, glacial acetic acid and acetone, slightly soluble in ether and carbon tetrachloride, and insoluble in gasoline. Its solutions in water and alcohol (96%) are colored yellow, in the other mentioned solvents colorless.

Only with the free semicarbazide in anhydrous alcohol solution were we able to obtain the nitrodimedon semicarbazone. Yellow crystals. M.p. 240-241°. Difficultly soluble in alcohol and ether, readily soluble in glacial acetic acid and in water.

4.357 mg sub.: 0.902 ml N_2 (23°, 746 mm). Found %: N 23.43. $C_9H_{14}O_4N_4$. Calculated %: N 23.14.

Nitrodimedon Phenylhydrazone. When an alcohol solution of nitrodimedon was boiled with phenylhydrazine two kinds of crystals were obtained (probably mono- and bis-phenylhydrazones). When the mixture is boiled with acetone the nitrodimedon monophenylhydrazone remains insoluble as red crystals with m.p. 222.5°.

2.657 mg sub.: 0.348 ml N_2 (20°, 764 mm). Found %: N 15.34. $C_{14}H_{17}O_3N_3$. Calculated %: N 15.27.

Yellow crystals were isolated from the acetone, the composition of which has not yet been determined.

Nitrodimedon Salts

Sodium Salt. An alcohol solution of nitrodimedon was boiled with sodium carbonate and filtered. The filtrate was diluted with ether. The sodium salt of nitrodimedon separated as yellow plates.

3.186 mg sub.: 0.165 ml N_2 (19°, 781 mm). Found %: N 6.22. $C_8H_{10}O_4NNa$. Calculated %: N 6.22.

Silver Salt. Prepared by the reaction of nitrodimedon with silver oxide in alcohol solution. When compared with other nitrodimedon salts it is less soluble in alcohol and on cooling its solution it separates as yellow glistening crystals.

3.857 mg sub.: 0.150 ml N_2 (15°, 764 mm). 0.1062 g sub.: 0.0519 g AgCl. Found %: N 4.63; Ag 36.71. $C_8H_{10}O_4NAg$. Calculated %: N 4.79; Ag 36.98.

Lead Salt. Prepared from nitrodimedon and lead oxide (in alcohol solution). Yellow plates.

2.271 mg sub.: 0.091 ml N_2 (19°, 757 mm). Found %: N 5.02 ($C_8H_{10}O_4N$)₂Pb. Calculated %: N 4.87.

Copper Salt. An alcohol solution of nitrodimedon was boiled with powdered copper oxide. After filtration the dark blue filtrate was diluted with ether. The salt separates as greenish cubes.

2.586 mg sub.: 0.137 ml N_2 (19°, 756 mm). Found %: N 6.16. ($C_8H_{10}O_4N$)₂Cu. Calculated %: N 6.49.

Cobalt Salt. Prepared the same as the preceding. The dilution with ether gave red crystals.

3.686 mg sub.: 0.192 ml N_2 (22°, 766 mm). Found %: N 6.07. ($C_8H_{10}O_4N$)₂Co. Calculated %: N 6.56.

Bivalent Iron Salt (Ferrous Salt). Prepared by boiling iron sulfide (FeS) with an alcohol solution of nitrodimedon. Forms dark purple crystals, dissolving in water with a dark-green color.

2.986 mg sub.: 0.174 ml N_2 (18°, 762 mm). Found %: N 6.85. ($C_8H_{10}O_4N$)₂Fe. Calculated %: N 6.60.

When heated the nitrodimedon salts fail to melt and instead decompose violently (with flashing). The least stable is the nitrodimedon silver salt.

Aniline Salt. When an ether solution of aniline is added to an alcohol solution of nitrodimedon the aniline salt of nitrodimedon is obtained as colorless needle crystals. M.p. 151°. Readily soluble in water.

3.786 mg sub.: 0.328 ml N_2 (19°, 772 mm). Found %: N 10.13. $C_{14}H_{18}O_4N_2$. Calculated %: N 10.07.

p-Toluidine Salt. Prepared the same as the aniline salt. Colorless crystals. M.p. 160°.

3.829 mg sub.: 0.326 ml N_2 (22°, 755 mm). Found %: N 9.79. $C_{15}H_{20}O_4N_2$. Calculated %: N 9.57.

β -Naphthylamine Salt. Prepared the same as the aniline salt. Colorless crystals. M.p. 153°.

3.843 mg sub.: 0.289 ml N_2 (23°, 757 mm). Found %: N 8.63. $C_{18}H_{20}O_4N_2$. Calculated %: N 8.54.

4-Nitro-4-chloro-1,1-dimethyl-3,5-cyclohexanedione (Chloronitrodimedon)
(V; X = Cl)

A solution of 1.5 g of nitrodimedon in 50 ml of water was treated with chlorine. A white precipitate separated. Filtered and washed with water. Yield nearly quantitative. Recrystallized from carbon tetrachloride. Colorless crystals. M.p. 121°.

2.200 mg sub.: 0.123 ml N_2 (23°, 766 mm). 5.057 mg sub.: 3.257 mg AgCl. Found %: N 6.50; Cl 15.93. $C_8H_{10}O_4NCl$. Calculated %: N 6.38; Cl 16.17.

4-Nitro-4-bromo-1,1-dimethyl-3,5-cyclohexanedione (Bromonitrodimedon)
(V; X = Br)

Obtained the same as the preceding from the dimedon and bromine water. Colorless crystals with m.p. 141°.

3.814 mg sub.: 0.166 ml N_2 (22°, 757 mm). 3.000 mg sub.: 2.114 mg AgBr. Found %: N 5.02; Br 29.98. $C_8H_{10}O_4NBr$. Calculated %: N 5.30; Br 30.30.

When heated with water both the chloronitrodimedon and the bromonitrodimedon revert back to nitrodimedon with the cleavage of hypochlorous or hypobromous acid. Both liberate iodine from potassium iodide solution. Both the chloro- and bromonitrodimedons are soluble in alcohol, benzene and carbon tetrachloride; slightly soluble in alcohol, benzene and carbon tetrachloride; slightly soluble in ether, and insoluble in water.

Bromonitrodimedon gives with indole in glacial acetic acid a brown color, at higher indole concentrations a brown precipitate separates.

SUMMARY

1. A method was developed for obtaining nitrodimedon by the nitration of dimedon with fuming nitric acid.
2. Some of the salts of nitrodimedon with inorganic and organic bases, readily soluble in water and in alcohol, were described.
3. The bromo- and chloro- derivatives of nitrodimedon were obtained.
4. The mono-semicarbazone and mono-phenylhydrazone of nitrodimedon were prepared.

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PREPARATION OF 4 (or 5) -IMIDAZOLYLMETHYL ESTERS OF 4 - AMINO AND 4 - BUTYLAMINO BENZOIC ACIDS

O. K. Nikiforova

In connection with the ever increasing needs of native medicine for histamine, used in the therapy of various ailments, the Western Siberian Affiliate of the Academy of Sciences of the USSR undertook the task of synthesizing histamine by a new method.

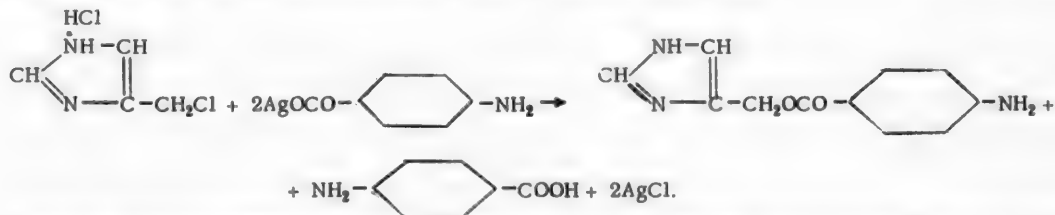
In contrast to the existing methods for the preparation of this compound, in the present case readily available invert sugar [1] was used as the crude for the synthesis. This method also makes it possible to obtain in the pure form and in any amount the earlier difficultly available intermediates: 4(or 5)-(hydroxymethyl) imidazole and 4(or 5)-(chloromethyl) imidazole.

As is known, the physiological activity of histamine for the most part depends on its imidazole grouping. Imidazole, as well as its simpler derivatives - 4(or 5)-methyl-imidazole, 4(or 5)-(hydroxymethyl) imidazole, 4(or 5)-(chloromethyl)-imidazole and others - produce to different degrees contraction in the isolated uterus and intestine, stimulate peristalsis and reduce blood pressure [7]. The coupling of the imidazole nucleus with the ethylamine radical explains the specific pain-killing action of histamine. The condensation of imidazole derivatives and 4-amino-benzoic acid with the formation of the ester grouping characteristic for compounds of the type of novocaine promised to give substances that could qualify as new local anesthetics.

With this in mind the 4(or 5)-imidazolylmethyl ester of 4-aminobenzoic acid and the 4(or 5)-imidazolylmethyl ester of 4-butylaminobenzoic acid were synthesized, the methods for the preparation of which is the subject of the present paper.

As starting products, containing the imidazole grouping, were used the intermediates in the synthesis of histamine, namely 4(or 5)-(hydroxymethyl) imidazole and 4(or 5)-(chloromethyl) imidazole. 4(or 5)-(Hydroxymethyl) imidazole was synthesized by the method of Kulev and Onishchuk [1]. 4(or 5)-(Chloromethyl) imidazole was obtained by the action of thionyl chloride on 4(or 5)-(hydroxymethyl)-imidazole [2].

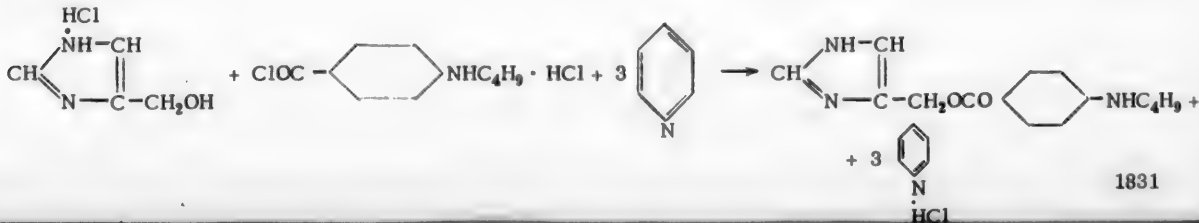
The condensation of 4(or 5)-(chloromethyl) imidazole with the silver salt of 4-aminobenzoic acid in anhydrous methyl alcohol gave the 4(or 5)-imidazolylmethyl ester of 4-aminobenzoic acid:



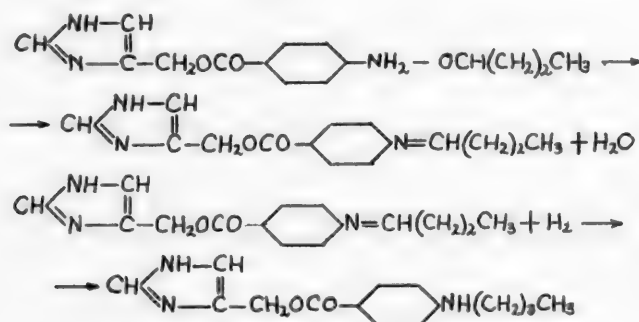
The silver salt of aminobenzoic acid was obtained in the same manner as the silver salt of 4-methylaminobenzoic acid [3].

We were unable to obtain the 4(or 5)-imidazolylmethyl ester of 4-butylaminobenzoic acid through the silver salt of 4-butylaminobenzoic acid. Instead it was obtained by two other methods:

a) condensation of 4(or 5)-(hydroxymethyl) imidazole with 4-butylaminobenzoyl chloride in anhydrous pyridine (method A):



b) butylation of the earlier obtained 4(or 5)-imidazolylmethyl ester of 4-aminobenzoic acid with butyraldehyde under simultaneous reduction of the azomethine formed in the butylation (method B):



The studies of Shapiro [4], Clinton [5] and others were used in developing the second method, which studies indicated the possibility of butylating certain esters of 4-aminobenzoic acid with butyraldehyde.

4-Butylaminobenzoic acid and the hydrochloride of butylaminobenzoyl chloride were synthesized by known methods [6].

The pharmacological studies, made at the Pharmacology Cathedra of the New Siberian Medical Institute, revealed that the obtained esters possess local anesthetic properties.

EXPERIMENTAL

1. 4(or 5)-(Chloromethyl)imidazole Hydrochloride

To 50 g of 4(or 5)-(hydroxymethyl)imidazole hydrochloride was added in the cold 86 ml of thionyl chloride. The flask was quickly connected to a bulb condenser, fitted with a calcium chloride tube. Vigorous reaction in the cold proceeded for 10 minutes, after which the evolution of gases almost ceased. The reaction mass was heated on the water bath at 80-85° for 40 minutes, and then the excess thionyl chloride was vacuum distilled. After the distillation there remained in the flask a yellow deposit of 4(or 5)-(chloromethyl)imidazole. The crude product was recrystallized from anhydrous ethyl alcohol under boiling with animal charcoal. Purification gave 43.6 g of 4(or 5)-(chloromethyl)imidazole hydrochloride with m.p. 139-140° (literature: 140-141°). Yield of pure product 77%.

2. Silver Salt of 4-Aminobenzoic Acid

To a hot solution of 35 g of 4-aminobenzoic acid in 1700 ml of distilled water was carefully added 12% ammonia solution until neutral to litmus. The solution was cooled to 35-40° and to it with vigorous stirring was added in portions a solution of 40 g of silver nitrate in 110 ml of water; here copious precipitation of the white silver salt was observed.

After cooling the flask to room temperature in a dark place the precipitate was filtered and washed several times with cold distilled water. The well pressed silver salt was dried in a vacuum desiccator over sulfuric acid or solid potassium hydroxide. To protect the silver salt from decomposition by light the vacuum desiccator was put in a dark place. Weight of dry silver salt of 4-aminobenzoic acid 49 g. Yield 79%.

3. 4(or 5)-Imidazolylmethyl Ester of 4-Aminobenzoic Acid

In a flask, fitted with a mercury seal stirrer, was placed 49 g of silver 4-aminobenzoate, 15.4 g of 4(or 5)-(chloromethyl)imidazole and 250 ml of anhydrous methyl alcohol. For avoiding the action of light and decomposition of the silver salt the flask was covered on the outside with black paper. Under constant mechanical stirring the reaction mixture was boiled on the water bath for 3.5 hours. After cooling to room temperature the reaction mixture was filtered and the obtained precipitate was washed several times with methyl alcohol. The filtrates were combined and the methyl alcohol was distilled off to a sirupy liquid as residue. The liquid was placed in a vacuum desiccator and in 12 hours congealed to a yellow glass. Then the product was treated in the cold with water under vigorous rubbing with a glass rod. The resulting yellow amorphous precipitate was filtered and for extracting the 4-aminobenzoic acid was treated several times with ether. The product dried at 50-60° melted in the range 186-190°.

Several recrystallizations from 50% ethyl alcohol gave 10.7 g of pure compound with m.p. 216°. Yield 49.1%.

The 4(or 5)-imidazolylmethyl ester of 4-aminobenzoic acid crystallizes as glistening white leaflets, insoluble in ether, difficultly soluble in cold water, moderately soluble in hot water, and readily soluble in ethyl and methyl alcohols.

When coupled with diazotized sulfanilic acid it gives a brownish-red color, characteristic for imidazole derivatives.

6.151, 6.502 mg sub.: 13.670, 14.469 mg CO₂; 2.869, 3.016 mg H₂O. Found %: C 60.65, 60.73; H 5.22, 5.19. C₁₁H₁₁O₂N₃. Calculated %: C 60.81; H 5.10.

4. 4(or 5)-Imidazolylmethyl Ester of 4-Butylaminobenzoic Acid

Method A. In a two-necked round bottomed flask, fitted with mercury seal and mechanical stirrer, was placed 90 ml of dry, freshly distilled pyridine and 8.2 g of 4(or 5)-(hydroxymethyl)-imidazole hydrochloride. The solution of the (hydroxymethyl) imidazole in the pyridine began at room temperature and was completed on heating the mixture to 30-40° on the water bath. To the thus obtained homogeneous solution was added in small portions 13 g of 4-butylaminobenzoyl chloride hydrochloride. Then the light brown solution was heated on the water bath with constant stirring for 6 hours. The temperature of the water bath was kept at 60-65° in the early hours, and at 95-100° toward the end. After cooling to room temperature the reaction mixture was poured into cooled 20% sulfuric acid solution. The obtained spongy precipitate was filtered, well washed with 20% soda solution, and then with water. Weight of precipitate 8.2 g. Melting point of the crude product 209-214°.

After several recrystallizations from ethyl alcohol the product melted at 234-234.5°. Weight of purified product 6.0 g. Yield 41%. 4(or 5)-Imidazolylmethyl 4-butylaminobenzoate is practically insoluble in cold water, difficultly soluble in hot water, and readily soluble in ethyl alcohol, alcohol-water mixture, benzene, pyridine and glacial acetic acid.

Method B. A mixture of 3.5 g of 4(or 5)-imidazolylmethyl 4-aminobenzoate and 3 ml of butyraldehyde was heated on the water bath for 1 hour. Then 15 ml of alcohol was added to the reaction mass, after which it was heated another 40 minutes. The reaction mixture was let stand 12-14 hours, after which 15 ml of glacial acetic acid and 5 g of zinc dust were added. The reduction was run for 3 hours with boiling on the water bath and mechanical stirring. At the end of reaction the mixture was filtered and the filtrate was poured into 100 ml of water and ice. The liquid was made alkaline to litmus with sodium carbonate solution, the precipitate was filtered, washed with cold water, and dried.

After recrystallization from alcohol the ester melted at 234°. Yield 2 g (46%).

6.985, 7.895 mg sub.: 16.855, 19.039 mg CO₂; 4.363, 4.974 mg H₂O. Found %: C 65.85, 65.81; H 6.99, 7.05. C₁₅H₁₉O₂N₃. Calculated %: C 65.91; H 7.01.

SUMMARY

1. The unknown 4(or 5)-imidazolylmethyl 4-aminobenzoate and 4(or 5)-imidazolylmethyl 4-butylaminobenzoate were synthesized.

2. The synthesis of 4(or 5)-imidazolylmethyl 4-aminobenzoate was realized by the condensation of 4(or 5)-(chloromethyl) imidazole with the silver salt of 4-aminobenzoic acid. 4(or 5)-imidazolylmethyl 4-butylaminobenzoate was obtained by two methods:

- a) condensation of 4(or 5)-(hydroxymethyl) imidazole with 4-butylaminobenzoyl chloride;
- b) butylation of 4(or 5)-imidazolylmethyl 4-aminobenzoate with butyraldehyde and reduction of the resulting azomethine.

3. The obtained esters possess local anesthetic properties.

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INVESTIGATION OF ORGANIC ISOCYANATES

IV. TRANSFORMATION OF PHENYL- AND 1-NAPHTHYLISOTHIOCYANATES BY TREATMENT

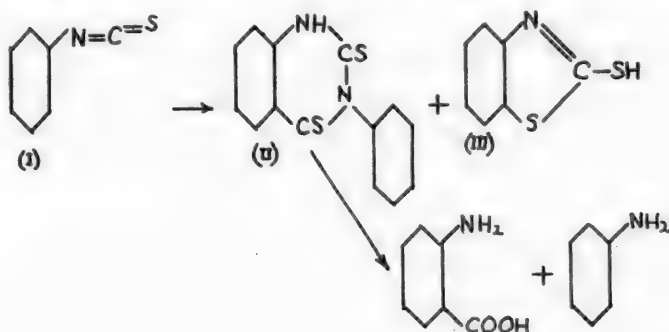
WITH ALUMINUM CHLORIDE

N. S. Dokunikhin and L. A. Gaeva

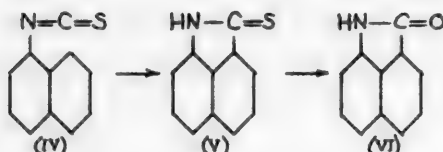
It was shown earlier that, by reaction with molten mixtures of aluminum chloride and sodium chloride, phenylisocyanate yields 3-phenyl-2,4-dioxotetrahydroquinazoline [1], but 1-naphthylisocyanate isomerizes to the lactam of 1,8-aminonaphthoic acid - naphthostyryl [2]. It is of interest to study the transformation of the corresponding isothiocyanates under similar conditions.

It is known that, with the aromatic hydrocarbons [3], and especially with the phenolic esters [4], in the presence of aluminum chloride, the organic isothiocyanates form substituted amides of thiocarboxylic acids, which are analogous to the substituted amides of carboxylic acids obtained from the isocyanates, according to Leuckart [5]. Observing the reaction of the phenyl derivative of mustard oil with benzene and aluminum chloride, Friedmann and Gattermann [3] isolated thiobenzanilide and a product that had a m.p. of 154°, was insoluble in alkali, contained one atom of sulfur to two molecules of phenylisothiocyanate, $(C_6H_5NCS)_2S$, and at the same time had an odor indicating the presence of phenylisocyanate. The authors showed the identity of the isolated substance with the compound that Proskauer and Sell [6] obtained by reaction of bromine and the phenyl derivative of mustard oil, followed by treatment with alcohol. Friedmann and Gattermann obtained the same substance without the use of benzene, by warming a mixture of the phenyl derivative of mustard oil and aluminum chloride for a period of 15 minutes on the water bath. The reaction of phenylisothiocyanate with aluminum chloride at higher temperatures was not described. From the products of the reaction of phenylisothiocyanate (I) with a molten mixture of aluminum chloride and sodium chloride, we isolated two substances that were soluble in aqueous alkali, and which could be separated by their different degrees of acidity as well as by chromatography.

One of them was identified as 2-mercaptobenzothiazole (III), and the other proved to be 3-phenyl-2,4-dithion-tetrahydroquinazoline (II). The structure of the latter was verified by analysis, by determination of the molecular weight, and by cleavage, using hot aqueous alkali, resulting in the formation of aniline and anthranilic acid.



By reaction of 1-naphthylisothiocyanate (IV) with a molten mixture of aluminum chloride and sodium chloride, we obtained the lactam of 1,8-aminonaphthoic acid - thionaphthostyryl (V), which was soluble in aqueous solutions of alkali at ordinary temperatures, and from which, on acidification, it was precipitated unchanged. By boiling with a 50% solution of potassium hydroxide, followed by heating with hydrochloric acid, the thionaphthostyryl (V) was transformed to naphthostyryl (VI):



When our work was already completed, a report of an American Patent of 1953 [7] appeared, concerning a method of obtaining naphthostyryl by reacting 1-naphthylisocyanate with aluminum chloride. This method differed from that which we described in 1951 [2] for carrying out the reaction with the use of organic solvents, particularly dichlorobenzene. In the text of the reference, the feasibility of obtaining naphthostyryl (VI) from 1-naphthylisothiocyanate (IV) was indicated; however, no mention was made of the formation of the thioanalogue of naphthostyryl (V). Apparently, the latter circumstance is explained by the conditions of treatment of the reaction mass employed by the American investigators (heating with an aqueous solution of alkali, followed by acidification), which as described above, leads to the transformation of thionaphthostyryl to naphthostyryl. Similar treatment of the products of the reaction of 1-naphthylisothiocyanate with aluminum chloride, conducted under conditions that we selected, also led directly to naphthostyryl.

EXPERIMENTAL

1. Reaction of Phenylisothiocyanate with Aluminum Chloride

Into a molten mixture of 160 g of aluminum chloride and 38 g of sodium chloride at 165°, 20 g of phenylisothiocyanate (I) was introduced, and the mixture was stirred for 1 hour at 165-170°. The reaction mixture was then poured into a mixture of ice and water, filtered, and the precipitate was transferred to a dilute solution of hydrochloric acid, and the phenylisothiocyanate not entering into the reaction was removed by steam-distillation. The residue, after distillation, was filtered and the precipitate was stirred with a 5% solution of potassium hydroxide. From the alkaline filtrate, a current of carbon dioxide precipitated at first (pH ≈ 9) 3-phenyl-2,4-dithiontetrahydroquinazoline (II), then precipitated a mixture of the latter with 2-mercaptobenzothiazole (III). The total weight of the products isolated from the alkaline solution was 5.17 g, for compound (II) - 2.04 g, and for compound (III) - 1.73 g.

For 3-phenyl-2,4-dithiontetrahydroquinazoline (II) - the light yellow, tapering crystals from benzene had a m.p. of 280-294° (with decomposition). They were highly soluble in benzene, chloroform and alcohol.

Found %: C 62.55, 62.37; H 3.94, 3.81; S 22.76, 23.07; N 10.23, 10.03. M (in camphor). 272, 282. $C_{14}H_{10}N_2S_2$.
Calculated %: C 62.22; H 3.70; S 23.70; N 10.37. M 270.

The 2-mercaptobenzothiazole (III), after recrystallization from alcohol, had a m.p. of 173-178°. With a sample of the known substance, it did not give a depression of the melting point.

Cleavage of 3-phenyl-2,4-dithiontetrahydroquinazoline. 1.2 g of the substance was refluxed with 12 ml of 25% aqueous potassium hydroxide. On cooling, the aniline was extracted with ether, filtered and acidified. We obtained 0.43 g of anthranilic acid. After recrystallization from water and chloroform, the m.p. was 144.2-145.2°. The mixture, containing a known amount of the substance (m.p. 144.4-145.2°), melted at 144.6-145.6°. 0.37 g of benzanilide with a m.p. of 161.2-162.1° was obtained by treatment of the ether layer with benzoyl chloride and aqueous alkali. A mixture with the known substance (m.p. 162.6-163.4°), melted at 161.8-163.1°.

2. Reaction of 1-Naphthylisothiocyanate with Aluminum Chloride

20 g of 1-naphthylisothiocyanate was introduced into a molten mixture of 160 g of aluminum chloride and 38 g of sodium chloride at 165-170°, and the mixture stirred at this temperature for 1 hour. Then the substance was poured into a mixture of ice and water, filtered, and washed with a dilute solution of hydrochloric acid and water. The residue was stirred at room temperature with 5% aqueous potassium hydroxide. Then it was filtered, and the filtrate was acidified with hydrochloric acid. Thionaphthostyryl, with an intense orangish-yellow color, was precipitated. The yield was 5.2 g (26%). After purification of the chloroform solution chromatographically with aluminum oxide, and after crystallization from benzene, the m.p. was 156.6-157.6°. The precipitate consisted of yellow needles. They were highly soluble in benzene and chloroform, but insoluble in water.

Found %: C 71.27, 71.55; H 3.83, 3.82; S 16.87, 17.47; N 6.78, 6.97. M (in camphor) 175, 191. $C_{11}H_7NS$.
Calculated %: C 71.35; H 3.78; S 17.29; N 7.56. M 185.

Transformation of thionaphthostyryl to naphthostyryl. 0.35 g of the substance was boiled for a period of 12 hours in 30 ml of 50% solution of potassium hydroxide, the mixture then diluted with 60 ml of water, filtered, hydrochloric acid added to the filtrate until the pH was 9, and the filtrate finally poured into a mixture of ice and hydrochloric acid. It was heated to boiling and filtered. On cooling the filtrate, light yellow flakes of naphthostyryl precipitated. The yield was 0.24 g (75.23%), and the m.p. was 180.2-181.2°; a mixture with the known substance (m.p. 180.0-181.2°), melted at 180.0-181.2°.

SUMMARY

1. The reaction of phenylisothiocyanate with aluminum chloride yielded 3-phenyl-2,4-dithiontetrahydroquinazoline and 2-mercaptobenzothiazole.

2. The reaction of 1-naphthylisothiocyanate with aluminum chloride yielded the lactam of 1,8-aminothiophthalic acid - thionaphthostyryl, was obtained.

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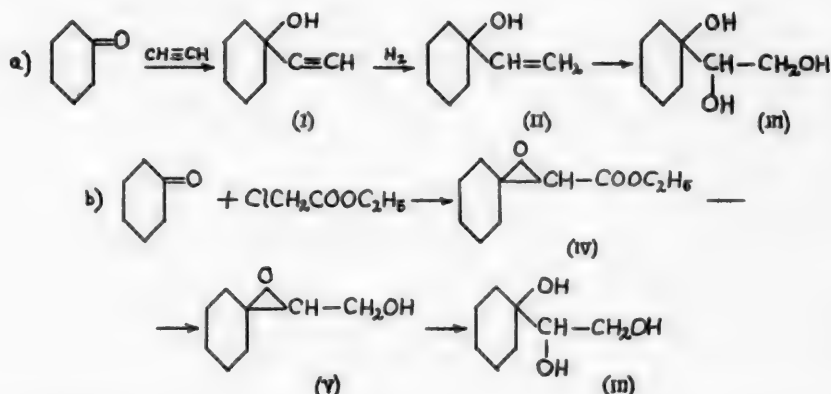
SYNTHESIS OF 1,1-PENTAMETHYLENGLYCEROL

A. Ya. Berlin and L. V. Sokolova

Only Azerbaev [1] has described 1,1-pentamethyleneglycerol [1-(1-hydroxycyclohexyl)-1,2-ethanediol] in the literature, having obtained it by the oxidation of 1-vinylcyclohexanol with potassium permanganate. However, the data given in this paper are extremely limited and do not permit judging the possibility of using the given method for preparing enough of the material in which we were interested.

Proceeding from cyclohexanone we outlined two methods for the synthesis of 1,1-pentamethyleneglycerol (III):

- via 1-ethynylcyclohexanol (I) and 1-vinylcyclohexanol (II) with subsequent oxidation of the latter, and
- via the ester of β,β -pentamethyleneglycidic acid (IV) and 3,3-pentamethyleneglycidol (V).

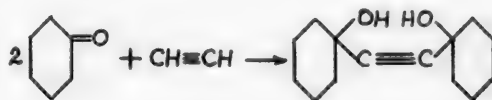


The performed experiments revealed that under definite conditions both of these schemes are practical.

A. Preparation of 1,1-Pentamethyleneglycerol via 1-Vinylcyclohexanol

Using the Favorsky method [2] we obtained 1-ethynylcyclohexanol (I) by the treatment of cyclohexanone with acetylene in ether in the presence of powdered potassium hydroxide. To obtain a good yield of the reaction product it is necessary to observe certain conditions.

First it is necessary to pass acetylene into the mixture of anhydrous ether and powdered potassium hydroxide for approximately an hour before beginning to add the cyclohexanone. Such saturation of the reaction medium with acetylene assures its presence in excess at the start of the reaction, which prevents the possibility of one mole of acetylene condensing with two moles of cyclohexanone to yield the compound bis(hydroxycyclohexyl)acetylene.



From this it follows that during the reaction process the cyclohexanone should be added quite slowly to the mixture of ether and powdered potassium hydroxide with constant passage of acetylene. After all of the cyclohexanone has been added it is recommended that the passage of acetylene be continued for some time until absorption ceases.

The potassium hydroxide used as condensing agent should be freshly ground, otherwise the carbonate film formed on its surface hinders reaction.

Constant vigorous stirring of the reaction mass is necessary, since it gradually thickens considerably in measure with reaction.

It is necessary to work up the reaction mixture the same day, immediately after termination of acetylene passage, since it was repeatedly noticed that if the reaction mass stood after the conclusion of ketone addition and acetylene passage (or was not kept sufficiently cool), then the yield of the acetylene alcohol was reduced and the yield of the corresponding glycol was increased. It is possible that this fact is explained by the reversible nature of the Favorsky reaction [3,4].

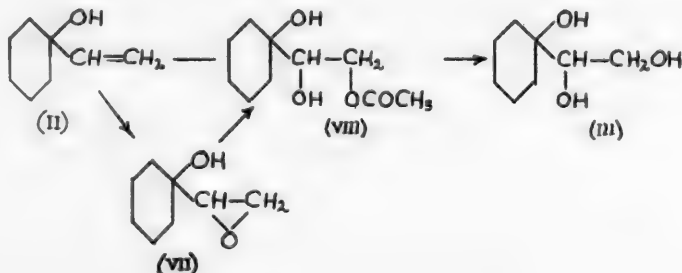
The yield of ethynylcyclohexanol with b.p. 62.5-63° at 8 mm and m.p. 31-32° was 89.5%. The total amount of by-product was only about 5% of the acetylene glycol - bis(1-hydroxycyclohexyl)-acetylene with m.p. 108.5-109°.

The method described by Nazarov and coworkers [5] was used for the selective hydrogenation of 1-ethynylcyclohexanol to 1-vinylcyclohexanol (II), consisting in the use of Pd-CaCO₃ as catalyst and termination of the hydrogenation process after one mole of hydrogen had been absorbed. The hydrogenation was run in anhydrous alcohol. As a result of the performed experiments it was revealed that the amount of catalyst, used by Nazarov and coworkers in analogous reactions, could be greatly reduced if the use of the catalyst was repeated several times without interruption (in the present case up to 6 times), adding to it only small amounts of fresh catalyst before each use. The hydrogenation of 1-ethynylcyclohexanol proceeds rapidly and quite smoothly without noticeable retardation of the reaction rate toward the end of absorbing 1 mole of hydrogen. The hydrogenation process was controlled at the end of reaction by the method of taking samples from the reaction mass and determining the presence of unreacted acetylene alcohol with the aid of ammoniacal silver nitrate solution. After 1 mole of hydrogen had been absorbed the reaction for the presence of the acetylene alcohol was negative. The yield of 1-vinylcyclohexanol with b.p. 65-66° at 11 mm was 84.8-85%.

The possibility was checked of selectively hydrogenating the ethynylcyclohexanol in the presence of spent skeletal nickel catalyst. The hydrogenation was run in alcohol solution; here it was established that selective hydrogenation of 1-ethynylcyclohexanol to 1-vinylcyclohexanol is not obtained with this catalyst; together with hydrogenation of the acetylene alcohol to the ethylene alcohol there also proceeds hydrogenation of the ethylene alcohol to the saturated alcohol. The tests with ammoniacal silver nitrate solution are positive for the presence of the acetylene alcohol during the whole hydrogenation process, i.e., clear up to the point where 2 moles of hydrogen are absorbed.

In order to obtain 1,1-pentamethyleneglycerol (III) from 1-vinylcyclohexanol we first of all checked the possibility of oxidizing the latter by the Wagner reaction using a cold acetone solution of potassium permanganate. However, it was revealed that under these conditions, together with oxidation, there proceeds considerable tarring, preventing the isolation of the desired product. We were able to isolate only a small amount of 1,1-pentamethyleneglycerol, which after repeated recrystallization from ethyl acetate melted at 113-114°. The yield of substance was exceedingly small; consequently we came to reject this method and turned to the attempted oxidation of 1-vinylcyclohexanol with peracetic acid. The oxidation of 1-vinylcyclohexanol with peroacids has not been reported before.

It is known that in the oxidation of olefins with an acetic acid solution of peracetic acid it is possible, depending on the reaction conditions, to isolate either the α -oxide, or the monoacetyl derivative of the glycol [6]. In the present case the possible transformations occurring in the oxidation of 1-vinylcyclohexanol and subsequent saponification of the reaction product can be depicted by the following scheme:



As a result, the intermediate products with this scheme should be the oxide of 1-vinylcyclohexanol (1,1-pentamethyleneglycidol) (VII) and the monoacetate of 1,1-pentamethyleneglycerol (VIII).

A solution of peracetic acid in glacial acetic acid was previously prepared from 27% hydrogen peroxide and acetic anhydride in the presence of concentrated sulfuric acid as catalyst [7]. This method is preferable to the method of obtaining peracetic acid without the use of catalyst, since when sulfuric acid is used the amount of extremely explosive diacetyl peroxide formed is usually exceedingly small.

The obtained acetic acid solution of peracetic acid was analyzed for the amount of hydrogen peroxide and peracetic acid. An extremely convenient and simple analysis method consists in the successive titration of the solution aliquot first with hydrogen peroxide and then with peracetic acid [8]. The possibility of titrating hydrogen peroxide in the presence of peracetic acid is conditioned by the fact that hydrogen peroxide is decomposed by permanganate at 0° and considerable dilution, while peracetic acid under these conditions remains unchanged and can later be determined iodometrically. The yield of peracetic acid was 87-89%.

We examined the oxidation of 1-vinylcyclohexanol with peracetic acid under various conditions. According to the data in the literature, sulfuric acid catalyzes the process of opening the α -oxide ring with acetic acid [7]. This circumstance was of interest to us for the reason that as the result of oxidizing 1-vinylcyclohexanol with the obtained, as indicated above, peracetic acid solution, containing sulfuric acid, it would be possible to immediately obtain the monoacetyl derivative of 1,1-pentamethyleneglycerol (VIII). However, as experiment revealed, under these conditions a complex mixture of products is formed, from which, despite repeated fractional distillation, we were unable to isolate any individual substances. Judging from the determination results for labile hydrogen, in the obtained fractions during reaction there simultaneously proceeds dehydration, which leads in the final end to the formation of a difficultly separated mixture of substances.

For this reason we subsequently ran the oxidation with an acetic acid solution of peracetic acid under the conditions where the sulfuric acid contained in the solution was previously neutralized with a solution of anhydrous sodium acetate in glacial acetic acid. This modification gave extremely favorable results. When the oxidation was run with peracetic acid solution, free of sulfuric acid, we obtained, depending on the experimental conditions, either 1,1-pentamethyleneglycidol (VII) or the monoacetyl derivative of 1,1-pentamethyleneglycerol (VIII) in excellent yields.

The oxidation of 1-vinylcyclohexanol was run for 1-2 hours at 20-25°; here it was revealed that if the reaction product was isolated immediately after the end of reaction the yield of 1,1-pentamethyleneglycidol, with b.p. 90-90.5° at 10 mm, was as high as 70%.

The conversion of 1,1-pentamethyleneglycidol into the monoacetyl derivative of 1,1-pentamethyleneglycerol is almost quantitative if the pure pentamethyleneglycidol is heated in glacial acetic acid at 70-80° for 9-10 hours. 1,1-Pentamethyleneglycerol monoacetate is a fairly viscous liquid with b.p. 126-127° at 2-3 mm.

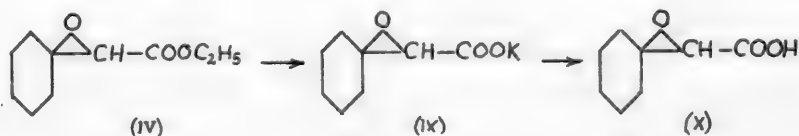
On the basis of the obtained results it can be concluded that it is possible to run the oxidation reaction without isolating the intermediate oxide. Actually, if after adding all of the 1-vinylcyclohexanol to the peracetic acid the whole reaction mixture is heated for 10-11 hours at 70-80°, then the monoacetyl derivative of 1,1-pentamethyleneglycerol is obtained. The yield of acetylated product obtained in this manner was 62-63%.

The monoacetate of 1,1-pentamethyleneglycerol under the influence of alcoholic sodium hydroxide is easily saponified to 1,1-pentamethyleneglycerol (III) with m.p. 113.5-114°.

B. Preparation of 1,1-Pentamethyleneglycerol via 3,3-Pentamethyleneglycidol

The ethyl ester of β,β -pentamethyleneglycidic acid (IV) was easily obtained by the Darzens condensation of cyclohexanone with chloroacetic ester in the presence of sodium ethylate [9].

The saponification of the ethyl ester with alcoholic potassium hydroxide gave the difficultly alcohol soluble potassium salt of β,β -pentamethyleneglycidic acid (IX), and from it the unknown free β,β -pentamethyleneglycidic acid (X) as crystals with m.p. 61-62°.



This acid proved to be extremely unstable. Attempts to recrystallize it failed, since here its melting point dropped considerably. After long standing in the air the acid became a tarry mass.

Next it was necessary to reduce the carboxy group to the carbinol group ($-\text{COOC}_2\text{H}_5 \rightarrow -\text{CH}_2\text{OH}$), without touching the α -oxide ring. Such catalysts as LiAlH_4 are frequently used for reducing the ester linkage to the alcohol. However, up to now this type of reaction has not been tried with glycidic esters. On the contrary, it is known [10] that under the influence of lithium aluminum hydride the α -oxide ring is easily cleaved in accord with the scheme:

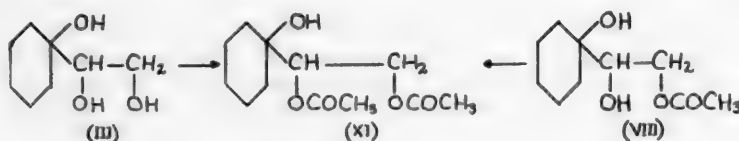


However, by running the reaction at extremely low temperature (-65°) we were able to effect the reduction of the β,β -pentamethyleneglycidic ester with lithium aluminum hydride to the 3,3-pentamethyleneglycidol (V) (b.p. $111-113^\circ$ at 8 mm) in yields up to 88.5%.

This interesting reaction, showing that under strong cooling the reduction of the ester grouping with lithium aluminum hydride proceeds with much greater ease than does the reductive cleavage of the α -oxide ring, may possibly also prove of value in other similar instances.

The hydrolytic cleavage of the α -oxide ring of 3,3-pentamethyleneglycidol (V) with the formation of 1,1-pentamethyleneglycerol (III) proceeded very smoothly under heating with 2% aqueous acetic acid.

Of the 1,1-pentamethyleneglycerol derivatives prepared the 2,3-diacetate (XI) was obtained by the action of acetic anhydride on the glycerol in pyridine at room temperature.



The same 1,1-pentamethyleneglycerol 2,3-diacetate is also formed in the acetylation of the monoacetyl derivative of pentamethyleneglycerol (VIII) under the same conditions.

EXPERIMENTAL

1-Ethynylcyclohexanol (I). In a three-necked flask, fitted with mercury seal stirrer, dropping funnel, tube for acetylene passage and outlet tube, was placed 1600 ml of anhydrous ether and then with stirring was added 210 g of freshly ground powdered dry potassium hydroxide. The mixture cooled to $-2 - 0^\circ$ was saturated with acetylene under stirring for 1-1.5 hours.

To the mixture with vigorous stirring was slowly added 98 g of freshly distilled cyclohexanone over approximately 3 hours, after which the passage of acetylene was continued for some time until absorption ceased. The temperature of the reaction mixture was maintained at $-1 - 0^\circ$ during the whole time of reaction. Then to the reaction mass was added 500-600 ml of water, the ether layer was separated, and the water layer was additionally ether extracted. The combined ether extracts were washed with a saturated sodium bisulfite solution, water, soda solution, again with water, and then dried over anhydrous sodium sulfate. After distilling off the ether the substance was vacuum distilled. The yield of 1-ethynylcyclohexanol (b.p. $62.5-63^\circ$ at 8 mm, m.p. $31-32^\circ$, n_D^{20} 1.4786) was 111 g, i.e., 98.5%.

A tarry mass remained in the flask after distillation, from which on addition of a small amount of ether was isolated 5.5 g of the bis(1-hydroxycyclohexyl)acetylene as a white crystalline substance with m.p. $105-107.5^\circ$. After recrystallization from petroleum ether, m.p. $108.5-109^\circ$ (literature m.p. $102-103^\circ$ [1]). The substance is readily soluble in acetone, alcohol and chloroform, difficultly soluble in benzene, and very difficultly soluble in water.

4.871 mg sub.: 13.400 mg CO_2 ; 4.302 mg H_2O . 3.730 mg sub.: 10.301 mg CO_2 ; 3.400 mg H_2O . Found %: C 75.54, 75.36; H 9.94, 10.20. $\text{C}_{14}\text{H}_{22}\text{O}_2$. Calculated %: C 75.63; H 9.98.

1-Vinylcyclohexanol (II). a) Hydrogenation in the Presence of Palladium Catalyst. To a solution of 24 g of

• All of the given melting points are corrected.

1-ethynylcyclohexanol in 45 ml of anhydrous ethyl alcohol was added 1 g of Pd-CaCO₃ (2% Pd) catalyst and the mixture was hydrogenated at room temperature and atmospheric pressure. After the absorption of 1 mole of hydrogen (5150 ml at 21° and 742 mm), for which about 2 hours was required, the hydrogenation was stopped. The catalyst was filtered and the solution was checked for the presence of unreacted acetylene alcohol in the reaction mixture. The test sample failed to give a precipitate with ammoniacal silver nitrate solution. The alcohol was distilled from the solution, while the residue was vacuum distilled. The yield of 1-vinylcyclohexanol was 20.7 g (84.8%), b.p. 65-66° at 11 mm, n_D^{20} 1.4738.

b) Hydrogenation in the Presence of Spent Skeletal Nickel Catalyst. To a solution of 8 g of 1-ethynylcyclohexanol in 30 ml of anhydrous ethyl alcohol was added 0.8 g of spent skeletal nickel catalyst and the mixture was hydrogenated at room temperature and atmospheric pressure. After 1 mole of hydrogen had been absorbed a test sample of the solution gave a voluminous gelatinous white precipitate when treated with ammoniacal silver nitrate solution. The presence of the starting acetylene alcohol continued to be shown even after the absorption of 120, 140, 160 and 180% of hydrogen. After the absorption of 2 moles of hydrogen (336 ml at 20° and 751.5 mm) a test sample of the solution failed to show reaction for the acetylene alcohol.

Oxidation of 1-Vinylcyclohexanol by Wagner. In a three-necked flask, fitted with stirrer, thermometer, dropping funnel and tube descending to the bottom, was placed a 2% solution of 5 g of 1-vinylcyclohexanol in acetone. With vigorous stirring and cooling of the solution to -1-0° there was slowly added dropwise a 2% solution of 5 g of potassium permanganate in acetone, containing the necessary amount of water for the reaction (2 ml). The addition of the permanganate required 8 hours with constant passage of carbon dioxide gas through the reaction mixture.

On conclusion of reaction the passage of carbon dioxide gas was continued for still some time to neutralize the formed alkali. The brown reaction mixture was filtered and the separated manganese dioxide was washed several times with acetone after which the solvent was distilled from the combined acetone solutions; here there remained a heavy dark amorphous mass, from which by treatment with hot ethyl acetate we were able to isolate a small amount of 1,1-pentamethyleneglycerol (III) as a white crystalline substance. After recrystallization from ethyl acetate the 1,1-pentamethyleneglycerol melted at 113-114° (literature [1] 104-105°). The substance is readily soluble in alcohol, acetone and water; soluble in hot ethyl acetate; difficultly soluble in benzene, ether and chloroform.

3.449 mg sub.: 7.592 mg CO₂; 3.091 mg H₂O. 3.979 mg sub.: 8.771 mg CO₂; 3.616 mg H₂O. Found %: C 60.07, 60.15; H 10.03, 10.15. C₈H₁₆O₃. Calculated %: C 59.98; H 10.07.

Peracetic Acid. In a three-necked flask, fitted with stirrer, thermometer, reflux condenser and dropping funnel, was placed 25.2 g of 27% hydrogen peroxide. To the well stirred hydrogen peroxide heated to 39-40° was cautiously added dropwise 124.7 g of acetic anhydride, containing 1% of concentrated sulfuric acid. The temperature of the reaction mass was maintained at 39-40° during the whole reaction, both by means of a cooling bath and by regulating the rate of acetic anhydride addition. The addition of the acetic anhydride took 1.5 hours. Based on its analysis [8] the yield of peracetic acid was 13.3 g, i.e., 87.6% based on hydrogen peroxide.

Oxidation of 1-Vinylcyclohexanol with Peracetic Acid in the Presence of Sulfuric Acid. To a solution of 13 g of peracetic acid, obtained as described, with vigorous stirring was added dropwise 18 g of 1-vinylcyclohexanol. The temperature of the reaction mass during reaction was maintained at 20-25°. In measure with vinylcyclohexanol addition the solution first became pink and then turned a brown color. On conclusion of reaction the mixture was analyzed for its peracetic acid content [8]. There was required 2.2 ml of 0.1 N Na₂S₂O₃ solution for titrating the iodine liberated by 1 ml of the solution.

The reaction mixture was poured into 10 volumes of water and exhaustively extracted with ether. The ether solution was washed with soda solution, water, and dried over anhydrous sodium sulfate. After removal of the solvent the product was repeatedly fractionally distilled in vacuo, where the following fractions were obtained: 1st) b.p. 43-44° at 12 mm; 2nd) b.p. 68-69.5° at 13 mm; 3rd) 86-87° at 13 mm; 4th) b.p. 102-103° at 13 mm.

1st Fraction:

4.042 mg sub.: 10.862 mg CO₂; 3.291 mg H₂O. 7.780 mg sub.: 0.43 ml CH₄ (15°, 755 mm). Found %: C 73.33; H 9.11; [H°] 0.18.

2nd Fraction:

3.123 mg sub.: 8.328 mg CO₂; 3.353 mg H₂O. 7.489 mg sub.: 20.009 mg CO₂; 8.891 mg H₂O. 7.61 mg sub.: 1.5 ml CH₄ (17°, 755 mm). Found %: C 72.77, 72.91; H 12.01, 11.95; [H°] 0.83.

3rd Fraction:

7.062 mg sub.: 18.594 mg CO₂; 6.419 mg H₂O. 3.787 mg sub.: 10.020 mg CO₂; 3.530 mg H₂O. 54.700 mg sub.:

4.89 ml CH_4 (17° , 755 mm). Found %: C 71.85, 72.20; H 10.17, 10.34; $[\text{H}^*]$ 0.37.

4th Fraction:

4.749 mg sub.: 12.428 mg CO_2 ; 4.359 mg H_2O . 3.032 mg sub.: 7.915 mg CO_2 ; 2.760 mg H_2O . 11.559 mg sub.: 0.47 ml CH_4 (18° , 755 mm). Found %: C 71.42, 71.24; H 10.27, 10.19; $[\text{H}^*]$ 0.17.

The results of these analyses did not permit us to judge as to the structure of the substances obtained in the given reaction. Only the low labile hydrogen content can be mentioned, which is evidence of partial dehydration.

1,1-Pentamethyleneglycidol (VII). For neutralization of sulfuric acid to the obtained, as indicated above, acetic acid solution of 13 g of peracetic acid was added a 20% solution of potassium acetate in glacial acetic acid until moist Congo paper failed to turn blue. To the well stirred peracetic acid solution was added dropwise over 2 hours 18 g of 1-vinylcyclohexanol. The temperature of the reaction mass during the whole time was maintained at $20-25^\circ$ with the aid of a cooling bath and by regulating the rate of vinylcyclohexanol addition. The solution remained colorless and clear to the reaction end. Heat evolution was observed for some time after all of the ethylene alcohol had been added.

On conclusion of reaction the mixture was analyzed for its peracetic acid content [8]. The titration of 1 ml of the solution required 2.5 ml of 0.1 N $\text{Na}_2\text{S}_2\text{O}_3$ solution.

The liquid was poured into 10 volumes of water, the solution saturated with sodium sulfate, and then extracted with ethyl acetate. The ethyl acetate extract was washed with sodium bicarbonate solution, water, and dried over anhydrous sodium sulfate. After removal of ethyl acetate the residual oil was vacuum distilled. Yield of 1,1-pentamethyleneglycidol with b.p. $90-90.5^\circ$ at 10 mm was 14.2 g (70%). 1,1-Pentamethyleneglycidol is a colorless mobile liquid, readily soluble in the ordinary organic solvents: ether, benzene, acetone, alcohol, xylene, chloroform and ethyl acetate, and difficultly soluble in water.

d_4^{18} 1.0605, n_D^{18} 1.4771, MR_D 37.90; calculated 37.91.

3.685 mg sub.: 9.114 mg CO_2 ; 3.300 mg H_2O . 15.790 mg sub.: 2.75 ml CH_4 (22° , 757 mm). Found %: C 67.50; H 10.02; $[\text{H}^*]$ 0.72. $\text{C}_8\text{H}_{14}\text{O}_2$. Calculated %: C 67.57; H 9.93; $[\text{H}^*]$ 0.71.

1,1-Pentamethyleneglycerol Monoacetate (VIII) From 1,1-Pentamethyleneglycidol. 1,1-Pentamethyleneglycidol (14.2 g) was heated with 7 parts of glacial acetic acid for 9-10 hours at $70-75^\circ$. After cooling the reaction mixture was poured into water, the solution was saturated with common salt, and then extracted with ethyl acetate. The ethyl acetate solution was washed with sodium bicarbonate solution, water, and then dried over anhydrous sodium sulfate. Removal of the solvent and vacuum distillation of the residue gave 17.95 g of the 1,1-pentamethyleneglycerol monoacetate with b.p. $126-127^\circ$ at 2-3 mm. Yield 88.8%. Pentamethyleneglycerol monoacetate is a colorless, viscous, oily liquid, readily soluble in the ordinary organic solvents and difficultly soluble in water.

$d_4^{19.5}$ 1.140, $n_D^{19.5}$ 1.4833, MR_D 50.69; calculated 50.86.

6.213 mg sub.: 13.445 mg CO_2 ; 4.970 mg H_2O . 3.377 mg sub.: 7.303 mg CO_2 ; 2.750 mg H_2O . 22.501 mg sub.: 5.2 ml CH_4 (16° , 751 mm). Found %: C 59.06, 59.07; H 8.95, 9.12; $[\text{H}^*]$ 0.97. $\text{C}_{10}\text{H}_{18}\text{O}_4$. Calculated %: C 59.38; H 8.97; $[\text{H}^*]$ 0.99.

1,1-Pentamethyleneglycerol Monoacetate (VIII) From 1-Vinylcyclohexanol. The oxidation of 1-vinylcyclohexanol with peracetic acid solution (after neutralization of the sulfuric acid) was run under the same conditions as described above for the preparation of 1,1-pentamethyleneglycidol. After adding 18.5 g of vinylcyclohexanol to a solution of 13.35 g of peracetic acid the reaction mixture was let stand overnight at room temperature, after which it was heated on the water bath at $70-80^\circ$ for 10-12 hours. The cooled liquid was poured into water, the solution was saturated with sodium sulfate, and then extracted with ethyl acetate. The separated ethyl acetate solution was washed with sodium bicarbonate solution, water, and dried over anhydrous sodium sulfate. After solvent removal the substance was distilled at $126-127^\circ$ and 2-3 mm. The yield of 1,1-pentamethyleneglycerol monoacetate was 18.4 g, or 62.1% based on taken vinylcyclohexanol.

1,1-Pentamethyleneglycerol (III) From the Monoacetate. To 2 g of 1,1-pentamethyleneglycerol monoacetate was added an alcoholic solution of 1.04 g of potassium hydroxide. The saponification was run for 12 hours at room temperature, in which connection the solution gradually turned yellow. After 12 hours the alcohol-alkali solution was acidified with an alcohol solution of hydrochloric acid to weakly acid to Congo, the potassium chloride was filtered and washed with alcohol, after which the alcohol was removed, while the residue was recrystallized from ethyl acetate. The yield of 1,1-pentamethyleneglycerol with m.p. $107.5-108^\circ$ was 0.79 g, which after 3 recrystallizations from ethyl acetate melted at $113.5-114^\circ$ and failed to depress the melting point when mixed with the pentamethyleneglycerol that had been obtained by the oxidation of 1-vinylcyclohexanol according to Wagner.

Potassium β,β -Pentamethyleneglycidate (IX). A solution of 6 g of the β,β -pentamethyleneglycidic ester (IV) [9] in anhydrous alcohol was added to an alcohol solution of 3.65 g of potassium hydroxide. Slight heating up of the reaction mixture was observed. The saponification of the ester was continued for 12-14 hours. Gradually the reaction mass turned yellow and there separated 6 g of the white potassium β,β -pentamethyleneglycidate. The salt was filtered, washed with alcohol and recrystallized twice from anhydrous alcohol. White lamellar crystals were obtained, insoluble in the cold in the ordinary organic solvents, difficultly soluble in cold alcohol and readily soluble in hot alcohol.

0.1497 g sub.: 0.0667 g K_2SO_4 . 0.3662 g sub.: 0.1627 g K_2SO_4 . Found %: K 20.0, 19.96. $C_8H_{11}O_3K$. Calculated %: K 20.08.

β,β -Pentamethyleneglycidic Acid (X). To a water solution of the potassium β,β -pentamethyleneglycidate was added with cooling a 1% hydrochloric acid solution to acid reaction to Congo. A white lustrous precipitate of β,β -pentamethyleneglycidic acid separated, which was filtered and dried in a vacuum desiccator; m.p. 61-62°. After recrystallization from aqueous methanol the melting point dropped to 46-47°. Long exposure to the air at room temperature transformed the β,β -pentamethyleneglycidic acid into a viscous, dark, tarry mass.

3,3-Pentamethyleneglycidol (V). In a three-necked flask, fitted with stirrer, reflux condenser, dropping funnel and thermometer, and protected from atmospheric moisture by means of calcium chloride tubes, was placed a solution of 15.76 g of ethyl β,β -pentamethyleneglycidate in anhydrous ether. The mixture was cooled to -65° by means of acetone-dry ice mixture. To the cooled solution with vigorous stirring was cautiously added dropwise a solution of 1.72 g of 95% lithium aluminum hydride in 245 ml of anhydrous ether. The ether solution was added at such a rate that the reaction mixture temperature stayed at -65° during the whole experiment. The addition of the lithium aluminum hydride solution required 2-2.5 hours. The mixture was let stand in the cooling bath, the temperature of which was gradually raised to -30°. The reaction mass was kept at this temperature for 1 hour. Then the temperature was raised to -10° and there was added 6 ml of ethyl acetate (for decomposing the excess lithium aluminum hydride), 48 ml of saturated ammonium chloride solution and several milliliters of water. The ether was separated, while the water solution was additionally ether extracted. The ether solution was dried over fused magnesium sulfate. After removal of solvent the residual oil was vacuum distilled.

There was obtained 10.75 g of substance with b.p. 120-123° at 10 mm, which corresponds to 88.5%. After a second distillation the b.p. was 116-117° at 9-10 mm. 3,3-Pentamethyleneglycidol is a mobile liquid without color or odor, soluble in the ordinary organic solvents and insoluble in water.

n_D^{17} 1.4823, d_4^{17} 1.0582, MR_D 38.33; calculated 37.91.

5.047 mg sub.: 12.525 mg CO_2 ; 4.475 mg H_2O . 3.297 mg sub.: 8.141 mg CO_2 ; 2.95 mg H_2O . 18.210 mg sub.: 3.14 ml CH_4 (22°, 752 mm). Found %: C 67.72, 67.39; H 9.92, 9.90; $[H^+]$ 0.71. $C_8H_{14}O_2$. Calculated %: C 67.57; H 9.92; $[H^+]$ 0.71.

1,1-Pentamethyleneglycerol (III) from 3,3-Pentamethyleneglycidol. To 1.55 g of 3,3-pentamethyleneglycidol was added 50 ml of 2% acetic acid solution with almost complete solution being observed. The mixture was heated for 1 hour on the boiling water bath and after cooling was ether extracted. Evaporation of the water gave 1.45 g of 1,1-pentamethyleneglycerol as white crystals. Yield 83%. After recrystallization from ethyl acetate the m.p. was 113-114°. The substance failed to depress the melting point when mixed with authentic 1,1-pentamethyleneglycerol.

1,1-Pentamethyleneglycerol 2,3-Diacetate from 1,1-Pentamethyleneglycerol. To a solution of 6 g of pentamethyleneglycerol in 60 ml of anhydrous pyridine was added 15.3 g of acetic anhydride. The mixture stood for 16 hours at room temperature, after which it was poured into 15 volumes of water. The solution was acidified with dilute hydrochloric acid until acid to Congo and then extracted with ether. The ether solution was washed with sodium bicarbonate solution, water, and dried over anhydrous sodium sulfate. After distilling off the ether there was obtained 7.48 g of substance with b.p. 127-128° at 2-2.5 mm.

1,1-Pentamethyleneglycerol 2,3-diacetate is a colorless, clear, viscous, oily liquid, readily soluble in the ordinary organic solvents and difficultly soluble in water.

n_D^{19} 1.4695, d_4^{19} 1.125, MR_D 60.50; calculated 60.25.

3.617 mg sub.: 7.853 mg CO_2 ; 2.708 mg H_2O . 16.996 mg sub.: 1.71 ml CH_4 (20°, 734 mm). Found %: C 59.25; H 8.37; $[H^+]$ 0.41. $C_{12}H_{20}O_6$. Calculated %: C 59.00; H 8.25; $[H^+]$ 0.41.

SUMMARY

1. The synthesis of 1,1-pentamethyleneglycerol was accomplished by two methods:

- a) from cyclohexanone via 1-ethynylcyclohexanol, 1-vinylcyclohexanol, 1,1-pentamethyleneglycidol and 1,1-pentamethyleneglycerol monoacetate;
- b) from cyclohexanone via the ethyl ester of β,β -pentamethyleneglycidic acid and 3,3-pentamethyleneglycidol.
2. On the example of converting the ethyl ester of β,β -pentamethyleneglycidic acid into 3,3-pentamethyleneglycidol it was shown that the esters of glycidic acids can be reduced by lithium aluminum hydride to the corresponding alcohols with retention of the α -oxide ring.

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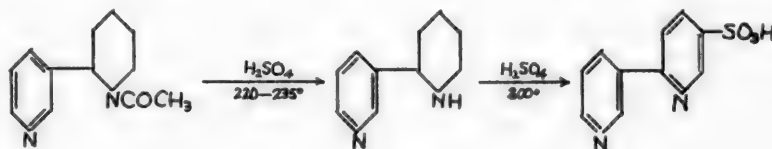
SYNTHESES BASED ON ANABASINE

IX. SULFONATION OF N-ACETYL- AND N-METHYLANABASINE WITH SULFURIC ACID

O. S. Otroshchenko and A. S. Sadykov

After the behavior of anabasine in its reaction with sulfuric acid [1] had been elucidated under the conditions used for pyridine sulfonation [2,3] it appeared of interest to study this reaction on some anabasine derivatives. The present paper communicates the study results obtained for the sulfonation of N-acetyl and N-methylanabasine.

The reaction of N-acetylanabasine with sulfuric acid under the conditions for the sulfonation of anabasine led to the formation of a crystalline product with acidic properties. A more detailed study revealed that the sulfonation of N-acetylanabasine proceeds in two stages – first the acetyl group is saponified and then, as in the case of anabasine, the 5-sulfonic acid of α, β -dipyridyl is obtained.



The sulfonation products of anabasine and N-acetylanabasine were identified as the nitriles (obtained from the sulfonic acid) and their derivatives. It should be mentioned that the reaction of N-acetylanabasine with sulfuric acid is much faster than the corresponding reaction for anabasine and the yield of product is slightly greater.

The experiments on the sulfonation of N-methylanabasine, made under the same conditions as for the sulfonation of anabasine and N-acetylanabasine, failed to give positive results. The reaction was accompanied by pronounced tarring and decomposition. Only volatile sulfur-containing products were isolated from the reaction mixture. The N-methylanabasine, as in the case of its electrochemical oxidation [4], proved to be less stable than anabasine to the action of sulfuric acid. Apparently, the presence of a methyl group on nitrogen lowers the stability of the piperidine ring. The negative experiments on the sulfonation of N-methylanabasine are indirect evidence of the fact that in the analogous reaction with anabasine the sulfonic group enters the dehydrogenated piperidine ring and the 5-sulfonic acid of α, β -dipyridyl is formed, i.e., the hydrogens of the piperidine ring fail to participate in the exchange reaction.

We made some additional studies on the properties of the 5-sulfonic acid of α, β -dipyridyl, which studies permitted us to elucidate some of its peculiarities when compared with β -pyridine-sulfonic acid. In contrast to the latter [3], the sulfonic group in α, β -dipyridyl-5-sulfonic acid is extremely stable. The exchange reactions proceed under more drastic conditions than in the case of β -pyridinesulfonic acid. Thus, for example, the fusion reactions with alkali and potassium cyanide do not proceed under conditions analogous to those required for β -pyridinesulfonic acid. The acid hydrolysis of α, β -dipyridyl-5-sulfonic acid, which we attempted under various conditions, could not be achieved. Apparently, the presence of a pyridyl radical in the para position influences the properties of the sulfonic group, endowing it with greater stability than it possesses in the pyridine ring.

A cursory attempt was made to obtain the corresponding amide from 5-cyano- α, β -dipyridyl by treating it with hydrogen peroxide [5]. This amide, being a derivative of nicotinamide, is of interest from the viewpoint of its physiological activity. However, the oxidation went further and the α, β -dipyridyl-5-carboxylic acid was formed instead.

EXPERIMENTAL

Acetylation of Anabasine. To 100 g of anabasine with cooling was gradually added 70 g of acetic anhydride. The resulting mixture was heated on the water bath for 12 hours. Then the reaction mass was dissolved in a small volume of water, saturated with soda, and extracted with chloroform. After drying over sodium sulfate and distilling off the

solvent the residual oil was distilled in vacuo. Two fractions were obtained: 1st fraction - b.p. 129-132° (2 mm), 15.6 g (anabasine); 2nd fraction - b.p. 159-160° (2 mm), 61.5 g, n_D^{20} 1.5530 (N-acetylanabasine). N-Acetylanabasine picrate has m.p. 184-185°.

Sulfonation of N-Acetylanabasine with Sulfuric Acid at 300°. Experiment 1. To 30 g of N-acetylanabasine with cooling was added 33 ml of sulfuric acid (d 1.84). The obtained mixture was heated at 300° on the sand bath for 4 hours. After cooling the reaction mixture was dissolved in water and boiled with barium carbonate for 1 hour. The filtrate after removal of the mixed barium sulfate-barium carbonate precipitate was evaporated to small volume on the water bath. On cooling the barium salt of α, β -dipyridyl-5-sulfonic acid separated. Weight 12.7 g (27.8%).

Experiment 2. To 15 g of N-acetylanabasine with cooling was added 16 ml of sulfuric acid (d 1.84). Heating of the mixture to 220° gave a small amount of distilled acetic acid (reaction with ferric chloride). Then the heating was continued at 300° for 10-12 hours. The reaction product was dissolved in water and boiled with barium carbonate. The filtrate after removal of the mixed barium sulfate-barium carbonate precipitate was boiled with animal charcoal. The solution was filtered and evaporated to small volume; cooling gave a precipitate. The yield of the barium salt of α, β -dipyridyl-5-sulfonic acid was 7.8 g (34.2%). α, β -Dipyridyl-5-sulfonic acid was obtained from the barium salt by decomposition with sulfuric acid.

62.791 mg sub.: 2.69 ml NaOH (0.09775 N). Found: equiv. 238.8. $C_{10}H_7SO_3H$. Calculated: equiv. 236.0.

Saponification of N-Acetylanabasine with Sulfuric Acid. To 5 g of N-acetylanabasine was added in small portions 5.5 ml of sulfuric acid (d 1.84). The mixture was heated at 220-235° for 4 hours, then it was dissolved in 65 ml of water, neutralized with 30% sodium hydroxide solution, and extracted with chloroform. After distilling off the chloroform an oil remained (3.1 g), from which a picrate with m.p. 200-201° was obtained. The mixed melting point with anabasine picrate was 202-203°.

5-Cyano- α, β -dipyridyl. A mixture of 1.5 g of the barium sulfonate, obtained from N-acetylanabasine, and 3 g of potassium cyanide was heated in a retort on the sand bath; here an oil distilled, solidifying in the retort tube. After recrystallization from benzene (or toluene) a substance with m.p. 106-108° was obtained. The mixed melting point with 5-cyano- α, β -dipyridyl failed to be depressed and was 106-108°.

5-Cyano- α, β -dipyridyl Picrate. The picrate with m.p. 180-181° was obtained by mixing alcohol solutions of the nitrile and picric acid. The mixed melting point with authentic 5-cyano- α, β -dipyridyl was 179-181°.

5-Cyano- α, β -dipyridyl Methiodide. To 0.1 g of the nitrile in 5 ml of anhydrous alcohol was added 0.1 g of methyl iodide. A precipitate separated from the solution on standing. The methiodide, recrystallized from methyl alcohol, has m.p. 242-243°. The mixed melting point with authentic 5-cyano- α, β -dipyridyl failed to be depressed and was 242-244°.

Oxidation of 5-Cyano- α, β -dipyridyl with Hydrogen Peroxide. To 1 g of 5-cyano- α, β -dipyridyl in 5 ml of alcohol was added 3.3 ml of 30% hydrogen peroxide and then (to the slightly warmed solution) 0.9 ml of 24% sodium hydroxide solution. A violent reaction ensued and the reaction mixture was cooled. Then the mixture was heated on the water bath for 1.5 hours and after cooling was neutralized with 5% sulfuric acid; here an acidic precipitate with m.p. 278-280° was obtained. The mixed melting point with α, β -dipyridyl-5-carboxylic acid failed to be depressed and was 279-280°.

SUMMARY

1. The sulfonation of N-acetyl- and N-methylanabasine was studied under the conditions used for the sulfonation of pyridine and anabasine. It was established that the sulfonation of N-acetylanabasine yields the α, β -dipyridyl-5-sulfonic acid. N-Methylanabasine when reacted with sulfuric acid suffers profound changes.
2. It was shown that at 220-235° the acetyl group in N-acetylanabasine is saponified by sulfuric acid.
3. The oxidation of 5-cyano- α, β -dipyridyl with hydrogen peroxide gives the α, β -dipyridyl-5-carboxylic acid.

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ALKYLATION IN WATER MEDIUM IN THE PRESENCE OF QUATERNARY AMMONIUM SALTS

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Quaternary ammonium salts, containing the radicals: benzyl [1], alkoxymethyl [2], indolylmethyl [3], 3-chlorobutenyl [4] and others, possess alkylating properties. This, apparently, is due to the ability of quaternary ammonium salts to suffer cleavage. As yet only solitary radicals are known that are capable of alkylation; however, this speaks only for the lower bond stability of these radicals with the ammonium nitrogen and says nothing about whether it is possible to accomplish this reaction (alkylation) with other radicals.

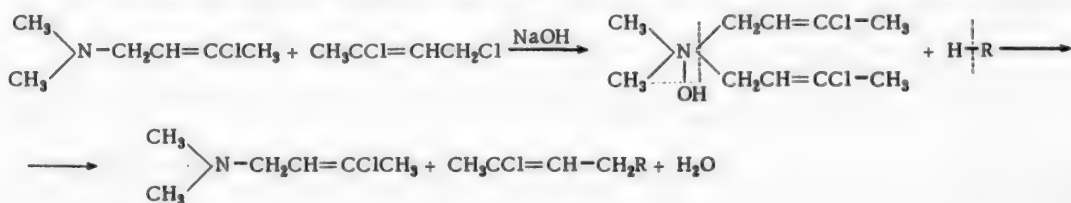
The excellent N-alkylation results obtained by us with dimethyldi(3-chlorobutenyl)ammonium chloride [4] permitted the hope that this salt would also prove to be a C-alkylation agent for compounds with labile hydrogen atoms. We subjected the compounds fluorene, naphthalene, phenylacetylene, malonic and acetoacetic esters to many hours of heating with dimethyldi(3-chlorobutenyl)ammonium chloride. The first two compounds under such heating remained unchanged and the only thing that happened in the reaction mixture was the earlier observed transformation of the dimethyldi(3-chlorobutenyl)ammonium chloride itself [5]. Phenylacetylene, malonic ester and acetoacetic ester actually underwent alkylation.

It seemed probable that alkylation would also proceed in alkaline medium, i.e., with quaternary ammonium bases. And since the formation of dimethyldi(3-chlorobutenyl)ammonium chloride from dimethyl(3-chlorobutenyl)amine and 1,3-dichloro-2-butene proceeds very rapidly, we deemed it possible to take it (the ammonium salt) in catalytic amounts and have in the reaction mixture a sufficient amount of 1,3-dichloro-2-butene so that the dimethyl(3-chlorobutenyl)amine liberated as the result of alkylation would immediately be bound by the 1,3-dichloro-2-butene with the repetitive formation of dimethyldi(3-chlorobutenyl)ammonium chloride. As a result, the tertiary amine would play the role of catalyst — a transfer agent for the chlorobutenyl radical.

Experiment completely justified our expectations. Acetoacetic ester in the presence of catalytic amounts of dimethyl-(3-chlorobutenyl)amine with the gradual addition of aqueous alkali is alkylated by 1,3-dichloro-2-butene. The yield of 3-chlorobutenylacetoacetic ester, based on the amount of acetoacetic ester taken, was 58%. The reaction proceeds smoothly and is complete after 15-25 minutes; acetylacetone also alkylates well, while malonic ester is alkylated in poorer yield. The replacement of 1,3-dichloro-2-butene by similarly constituted alkyl halides — allyl bromide and benzylchloride — failed, as was to be expected, to change the result.

It was shown by Knunyants [6] that the alkylation of acetoacetic ester with dialkyl sulfates can be run in water medium; for this reason we ran some control experiments on the alkylation of acetoacetic ester with 1,3-dichloro-2-butene in water medium in the absence of dimethyl(3-chlorobutenyl)amine. The (3-chlorobutenyl)acetoacetic ester was formed in an 18% yield of the theoretical. This sharp difference in yields clearly speaks for the catalytic influence exerted by the tertiary amine.

We assumed that also under these conditions the alkylation proceeds through the quaternary compound and that we are dealing with a reaction that is analogous to Hofmann reaction for the cleavage of quaternary bases, the only difference being that the hydrogen is taken not from the cleaved radical (which leads to an unsaturated compound) but from the compound with labile hydrogen atom that is present in the reaction mixture, which leads to its alkylation:



However, as further studies revealed, our representations on the reaction mechanism proved to be at variance with actuality, although they led us to some positive results.

Desiring to confirm the reaction mechanism adopted by us for alkylation in aqueous medium, we ran an experiment on the alkylation of acetoacetic ester with an aqueous solution of dimethyldi(3-chlorobutenyl)ammonium hydroxide without the addition of alkyl halide. The alkylation of acetoacetic ester failed to proceed under these conditions. The original postulation that the presence of a large amount of ammonium base in some way hinders alkylation was not confirmed: the presence of an equimolar amount of the ammonium base fails to hinder alkylation by the alkyl halide.

Later, in order to verify if the alkylation proceeds through the quaternary compound, we ran the following two experiments: 1) alkylation of acetoacetic ester with 1,3-dichloro-2-butene in the presence of an equimolar amount of dimethyldibenzylammonium chloride, and 2) alkylation of acetoacetic ester with benzyl chloride in the presence of an equimolar amount of dimethyldi(3-chlorobutenyl)ammonium chloride.

In the first experiment we obtained the pure (chlorobutenyl)acetoacetic ester (and its decomposition product - 6-chloro-5-hepten-2-one), and in the second - pure benzylacetoacetic ester (and its decomposition product - benzylacetone).

The results of these two experiments show that acetoacetic ester is alkylated only by the added alkyl halide. The alkyl radicals, present in the quaternary salt, do not participate in the alkylation (under these conditions).

In the literature we found one reference to the catalytic influence of quaternary ammonium salts in the synthesis of esters and derivatives of benzyl cyanide [7]. The author of these studies postulates that in these reactions there are formed, as intermediates, compounds that are analogous to those isolated by Schlenk and Holtz [8], namely, organic tetraalkylammonium derivatives. It seems very probable to us that a quaternary ammonium salt in alkaline medium forms with the alkylating compound an intermediate tetraalkylammonium derivative, which, similar to the analogous sodium derivative, reacts further with the added alkyl halide.

EXPERIMENTAL

Alkylation with Dimethyldi(3-chlorobutenyl)ammonium Chloride

Fluorene. A mixture of 16.6 g (0.1 mole) of fluorene and 25.9 g (0.1 mole) of dimethyldi(3-chlorobutenyl)ammonium chloride was heated for 30 hours at 160-170°. Then the reaction mixture was diluted with water and extracted with ether. The ether extract was dried over calcium chloride and after distilling off the solvent the residue was vacuum distilled. There was obtained 15.8 g of crystals, melting at 110-112°, and in mixture with fluorene at 111-113°. The water layer was made alkaline and washed with ether. The ether extract after distilling off the ether was distilled. There was obtained 3.7 g of dimethyl-(chlorobutenyl)amine and 3.1 g methyl-di(chlorobutenyl)amine [5], the picrate of the latter melts at 114-115° and fails to depress the melting point when mixed with the picrate of methyl-di(chlorobutenyl)amine. The gas liberated in the alkalization of the water layer was passed into dilute hydrochloric acid, which was then evaporated. The residue, recrystallized from alcohol, melts at 271-273° and fails to depress the melting point when mixed with trimethylamine hydrochloride.

Naphthalene. A mixture of 12.8 g of naphthalene (0.1 mole) and 25.9 g (0.1 mole) of dimethyldi(3-chlorobutenyl)ammonium chloride was heated for 48 hours at 170-175°. As the result of treatment, analogous to the preceding, there was obtained 11.7 g of naphthalene and the transformation products of the quaternary salt.

Phenylacetylene. A mixture of 10.2 g (0.1 mole) of phenylacetylene and 25.9 g (0.1 mole) of dimethyldi(3-chlorobutenyl)ammonium chloride was heated for 14 hours at 160-165°. The reaction mixture was diluted with water, extracted with ether, and after distilling off the solvent was vacuum distilled. There was obtained 7.9 g (fraction with b.p. 42-50° at 14 mm) of unreacted phenylacetylene and 7.4 g of a liquid with b.p. 163-166° at 14 mm, failing to give a precipitate with ammoniacal silver nitrate solution.

0.1019 g sub.: 0.1227 g AgCl. Found %: Cl 29.80. $C_{20}H_{21}Cl_3$. Calculated %: Cl 28.98.

The obtained compound, apparently tri(3-chlorobutenyl)phenylacetylene, was not studied closer.

From the water layer was obtained 1 g of dimethyl(chlorobutenyl)amine and 3.2 g of methyl-di(chlorobutenyl)amine (b.p. 222-230° at 680 mm), the picrate of which melts at 114-115°.

Malonic Ester. A mixture of 11.4 g (0.07 mole) of malonic ester and 20.7 g (0.08 mole) of dimethyldi(3-chlorobutenyl)ammonium chloride was heated for 14 hours at 170-180°.

There was obtained 3.9 g (22.6%) of the (chlorobutenyl)malonic ester (b.p. 165-168° at 19 mm), possessing after a second distillation the following constants:

b.p. 144.5-145° (11 mm), d_4^{16} 1.1093, n_D^{16} 1.4523.

From the literature [9]: b.p. 121.5-122.5° (6 mm), d_4^{16} 1.1059, n_D^{16} 1.4536.

Acetoacetic Ester. A mixture of 26 g (0.2 mole) of acetoacetic ester and 51.7 g (0.2 mole) of dimethyldi(3-chlorobutenyl)ammonium chloride was heated for 14 hours at 155-160°.

There was obtained 16.1 g (b.p. 144-147° at 16 mm) of the (chlorobutenyl)acetoacetic ester of 37.0%, based on taken acetoacetic ester. Part of this fraction was decomposed to the ketone. There was obtained the 6-chloro-5-hepten-2-one with b.p. 189-192° at 680 mm, and giving the semicarbazone with m.p. 123-125°.

From the literature [10]: b.p. 188-190°, semicarbazone m.p. 125-126°.

Alkylation in Water Medium

(Chlorobutenyl)acetoacetic Ester. To a vigorously stirred mixture of 26 g (0.2 mole) of acetoacetic ester, 27.5 g (0.22 mole) of 1,3-dichloro-2-butene and 2.7 g (0.02 mole) of dimethyl(chlorobutenyl)amine, heated on the water bath, was added over 20 minutes a solution of 12 g of potassium hydroxide in 20 ml of water. The heating was continued another 5 minutes. The top layer and the ether extract of the lower layer were dried over calcium chloride, and after distilling off the solvent, were distilled in vacuo. There was obtained 5.8 g of unreacted acetoacetic ester and 25.5 g (b.p. 127-137° at 8 mm) of the (chlorobutenyl)acetoacetic ester, the ketonic decomposition of which gave 10.1 g (34.4%) of 6-chloro-5-hepten-2-one, boiling at 189-192° and giving a semicarbazone with m.p. 123-125° [10].

The yield of (chlorobutenyl)acetoacetic ester, based on taken acetoacetic ester, was 58.3%, and 75.1%, based on reacted acetoacetic ester.

The water layer was acidified with hydrochloric acid and again extracted with ether. Nothing was found in the ether extract.

Under analogous conditions in the presence of 0.002 mole of catalyst the yield of (chlorobutenyl)acetoacetic ester was 46.0%, in the absence of catalyst it was 18.4%.

(Chlorobutenyl)acetylacetone. To a vigorously stirred mixture of 2.7 g (0.02 mole) of dimethyl(chlorobutenyl)amine, 2.5 g (0.02 mole) of 1,3-dichloro-2-butene and 20 g (0.02 mole) of acetylacetone on the water bath was added over 30 minutes 25 g (0.2 mole) of 1,3-dichloro-2-butene and 11.2 g of potassium hydroxide in 15 ml of water. Heating was continued for another 30 minutes. There was obtained 5.9 g of unreacted acetylacetone and 20.3 g (b.p. 110-115° at 6 mm) of (chlorobutenyl)acetylacetone, possessing after a second distillation the following constants:

B.p. 108-109° (4 mm), d_4^{20} 1.0967, n_D^{20} 1.489, M_R^D 49.6. $C_9H_{13}O_2Cl$. Calculated: 48.18.

0.1028 g sub.: 0.0776 g AgCl. Found %: Cl 18.68. $C_9H_{13}O_2Cl$. Calculated %: Cl 18.3.

The yield of (chlorobutenyl)acetylacetone was 54%, based on taken acetylacetone, and 77.3%, based on consumed acetylacetone.

(Chlorobutenyl)malonic Ester. To a vigorously stirred mixture of 5.4 g (0.04 mole) of dimethyl(chlorobutenyl)amine, 55 g (0.44 mole) of 1,3-dichloro-2-butene and 64 g (0.4 mole) of malonic ester on the water bath was added over 20 minutes a solution of 24 g of potassium hydroxide in 40 ml of water. Heating was continued for another 5 minutes.

There was obtained 25.77 g (b.p. 185-193° at 680 mm) of unreacted malonic ester and 29.92 g (b.p. 144-150° at 10 mm) of (chlorobutenyl)malonic ester, possessing the following constants [9]:

B.p. 144.5-145° (11 mm), d_4^{16} 1.1093, n_D^{16} 1.4523.

The yield of (chlorobutenyl)malonic ester was 30.1%, based on taken malonic ester, and 50.4%, based on consumed malonic ester.

Allylacetoacetic Ester. a) To a vigorously stirred mixture of 26 g (0.2 mole) of acetoacetic ester, 2.7 g (0.02 mole) of dimethyl(chlorobutenyl)amine and 26.7 g (0.2 mole) of allyl bromide on the water bath was added over 20 minutes a solution of 12 g of potassium hydroxide in 20 ml of water. Heating was continued for another 5 minutes.

There was obtained 22.44 g (b.p. 196-206° at 680 mm) of allylacetoacetic ester (66%, based on taken acetoacetic ester), the ketonic decomposition of which gave allylacetone, b.p. 124-126° at 680 mm, giving a semicarbazone with

m.p. 96-97° (literature [11], b.p. 129.6°; m.p. of semicarbazone 99-100°).

b) Under similar conditions without catalyst there was obtained 16.24 g (b.p. 195-205° at 680 mm) of the allyl-acetoacetic ester (47.7%, based on taken acetoacetic ester), the ketonic decomposition of which gave allylacetone, giving a semicarbazone with m.p. 94-96°.

Benzylacetoacetic Ester. a) To a vigorously stirred mixture of 2.7 g (0.02 mole) of dimethyl(chlorobutenyl)amine, 2.53 g (0.02 mole) of benzyl chloride and 26 g (0.2 mole) of acetoacetic ester on the water bath was added over 25 minutes 25.3 g of benzyl chloride and 12 g of potassium hydroxide in 20 ml of water. Heating was continued for another 35 minutes.

The following fractions were obtained (at 8 mm): 1st) 80-85°, 8.3 g; 2nd) 85-145°, 1.8 g; 3rd) 145-150°, 22.0 g; 4th) 205-213°, 6.1 g.

To the 1st fraction was added aqueous alkali solution. A voluminous precipitate separated. Then water was added and the mixture was extracted with ether. There was obtained 3.5 g of pure benzyl chloride.

The fraction with b.p. 145-150° (at 8 mm) distilled at 274-276° at atmospheric pressure (680 mm).

Prolonged standing of this fraction with aqueous ammonia gave needlelike crystals, after recrystallization from water melting at 149-150°. The m.p. given in the literature [12] for benzylacetoacetic ester is 283-284°. With ammonia the benzylacetoacetic ester gives the amide of benzylacetoacetic acid, melting at 150-151°.

The yield of benzylacetoacetic ester was 52.2%, based on taken acetoacetic ester, and 64.4%, based on consumed acetoacetic ester.

The use of benzyl iodide instead of the chloride failed to significantly affect the yield of the benzylacetoacetic ester.

b) Under analogous conditions without catalyst the yield of benzylacetoacetic ester was 32.3%, based on taken acetoacetic ester, and 42%, based on consumed acetoacetic ester.

Acetoacetic Ester and Dimethyldi(3-chlorobutenyl)ammonium Hydroxide. To a solution of 51.7 g (0.2 mole) of dimethyldi(3-chlorobutenyl)ammonium chloride in 12 ml of water was added a solution of 12 g of potassium hydroxide in 20 ml of water. Then 26 g (0.2 mole) of acetoacetic ester was added and the reaction mixture was stirred for 25 minutes on the water bath. There was obtained 20.0 g of pure acetoacetic ester with b.p. 69-72° (8 mm). Acidification of the water layer and ether extraction gave another 0.8 g of acetoacetic ester.

Alkylation of Acetoacetic Ester in the Presence of an Equimolar Amount of Dimethyldi(3-chlorobutenyl)ammonium Hydroxide. To a solution of 51.7 g (0.2 mole) of dimethyldi(3-chlorobutenyl)ammonium chloride in 12 ml of water was added a solution of 12 g of potassium hydroxide in 20 ml of water. Then was added 25 g (0.2 mole) of 1,3-dichloro-2-butene and 26 g (0.2 mole) of acetoacetic ester. To the obtained mixture with vigorous stirring on the water bath was added over 15 minutes a solution of 12 g of potassium hydroxide in 20 ml of water. Heating was continued for another 10 minutes.

There was obtained 24.5 g of (chlorobutenyl)acetoacetic ester with b.p. 114-124° at 5 mm (56.1%, based on taken acetoacetic ester).

Alkylation of Acetoacetic Ester with 1,3-Dichloro-2-butene in the Presence of an Equimolar Amount of Dimethylbenzylammonium Chloride. To 52.3 g (0.2 mole) of dimethylbenzylammonium chloride was added a solution of 9 g of sodium hydroxide in 40 ml of water. To the obtained solution was added 26 g (0.2 mole) of acetoacetic ester and 25 g (0.2 mole) of 1,3-dichloro-2-butene. To the vigorously stirred mixture on the water bath was added over 20 minutes a solution of 12 g of potassium hydroxide in 20 ml of water. Heating was continued for another 5 minutes.

There was obtained 18.2 g (41.6%) of the (chlorobutenyl)acetoacetic ester (b.p. 125-135° at 7 mm) and 2.4 g (8.2%) of 6-chloro-5-hepten-2-one, which distilled without vacuum in the range 187-196° and which gave a semicarbazone with m.p. 123-125°.

Alkylation of Acetoacetic Ester with Benzyl Chloride in the Presence of an Equimolar Amount of Dimethyldi(3-chlorobutenyl)ammonium Chloride. To a solution of 51.7 g (0.2 mole) of dimethyldi(3-chlorobutenyl)ammonium chloride was added a solution of 9 g of sodium hydroxide in 20 ml of water. To the obtained base was added 26 g (0.2 mole) of acetoacetic ester and 25.3 g (0.2 mole) of benzyl chloride. To the obtained mixture, vigorously stirred on the water bath, was added over 20 minutes a solution of 12 g of potassium hydroxide in 20 ml of water. Heating was continued for another 5 minutes.

There was obtained 15.8 g (35.9%) of benzylacetoacetic ester (b.p. 132-142° at 4 mm) and 3.6 g (12.2%) of benzylacetone (b.p. 223-228° at 680 mm), giving a semicarbazone with m.p. 142°. The literature [13] m.p. for benzylacetone semicarbazone is 142°.

SUMMARY

1. In the presence of catalytic amounts of quaternary ammonium salts it is possible to affect alkylation of compounds, containing a labile hydrogen, with alkyl halides in water medium under the influence of aqueous alkali.
2. The alkylation proceeds exclusively on the basis of the added alkyl halide. Under our conditions the alkyl radicals, present in the taken quaternary ammonium salt, fail to participate in the alkylation.
3. In its mechanism this alkylation reaction is completely different from the reaction mechanism for the alkylation of quaternary ammonium salts in nonaqueous media at elevated temperatures.

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IN MEMORIUM ROBERT KARLOVICH EIKHMAN

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On October 30, 1950 R. K. Eikhman died; Doctor of Technical Sciences, one of the greatest specialist and organizers of the aniline dye industry.

Robert Karlovich was born in 1879 in the home of a public teacher, in the village Lesnoi Karamysh of the Saratov district. After completing high school R. K. was a grammar school teacher for three years. In 1907 R. K. received a Chemical Engineering Degree and joined the Joint-Stock Company Plant in Moscow (later the Derbenevsk Plant). From the autumn of 1914 R. K. was the director of this plant, and after the nationalization of the latter in 1919 he became the first chosen Red director of this plant. The outstanding role played by R. K. in developing the plant during this time is covered in a feature article appearing in the November 30, 1922 issue of the newspaper "Pravda". In 1923 he occupied one of the first places in the number of 12 directors recognized by decree of the All-Russian jury under Chairman Mary Il'inichny Ulyanova ("Pravda" newspaper of February 9, 1923).

In 1919 R. K. was chosen a member of the committee for the administration of the aniline dye industry and assumed in succession the duties of Head of the Technical Section, Chairman of the Technical Committee of the industry and Substitute Director.

Up to 1925 R. K. also retained his directorship duties at the Derbenevsk plant. From 1925 to 1938, remaining on directive work in the Supreme administration of the industry, R. K. devoted great attention to the operation of the Central Laboratory of the industry and to the Experimental Plant; only from 1938, after a serious illness, was R. K. forced to limit his work to the confines of the industry's institute (the K. E. Voroshilov Scientific Institute of Organic Intermediates and Dyes).

The services of R. K. in developing the native industry are exclusively great. Even in the First World War, in 1915, R. K. organized in Moscow the production of phenol, picric acid and trotyl (trinitrotoluene) — materials that were deficient at the time and extremely important products in time of war. During these years, R. K. acted as consultant on the design, construction and familiarization with the production of these products at the plants near Moscow, in the Don Basin and around Petrograd.

In the period after the Great October Socialistic Revolution R. K. again entered into the role of director and organizer of many new Soviet industries.

As far as the more important achievements of R. K. are concerned, mention should be made of the original and highly productive method created by him for the production of phenol, which method, together with other methods, is used in our plants. Of no less significance for the national economy were the investigations of R. K. on the fractional separation of the coal tars from the Don and Kuznets Basins, and especially the work done on the anthracene-containing fractions. R. K. discovered and introduced into industry the dye-colored dyes, which are widely used in the textile industry (newspaper "Izvestiya" of February 15, 1939).

The researches of R. K. bore important significance for aniline, 2-naphthol, sulfur black, many kinds of sulfur dyes, anthraquinone, benzidine, alizarin and many others.

A great service of R. K. was the organization of laboratories at the plants of the aniline dye industry, which laboratories were capable of conducting original independent studies. On the problems of organic raw materials, chemistry and technology of intermediates and dyes, R. K. published about 20 papers, in which number are included several patents.

For a number of years R. K. directed the studies of diploma candidates at the D. I. Mendeleev Moscow Chemical-Technological Institute. Many of the industry's leaders are students of R. K.

The great services of R. K. in the industry were recognized in 1935 by decree of the People's Commissar of Heavy Industry and in 1939 by the People's Commissar of the Chemical Industry. In 1953 R. K. was rewarded by the Presidium of the Supreme Council of the USSR with the Order of Lenin.

The name of Robert Karlovich Eikhman, dear to all workers in the aniline dye industry, will go down in the history of the creation and development of the Soviet aniline dye industry.

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